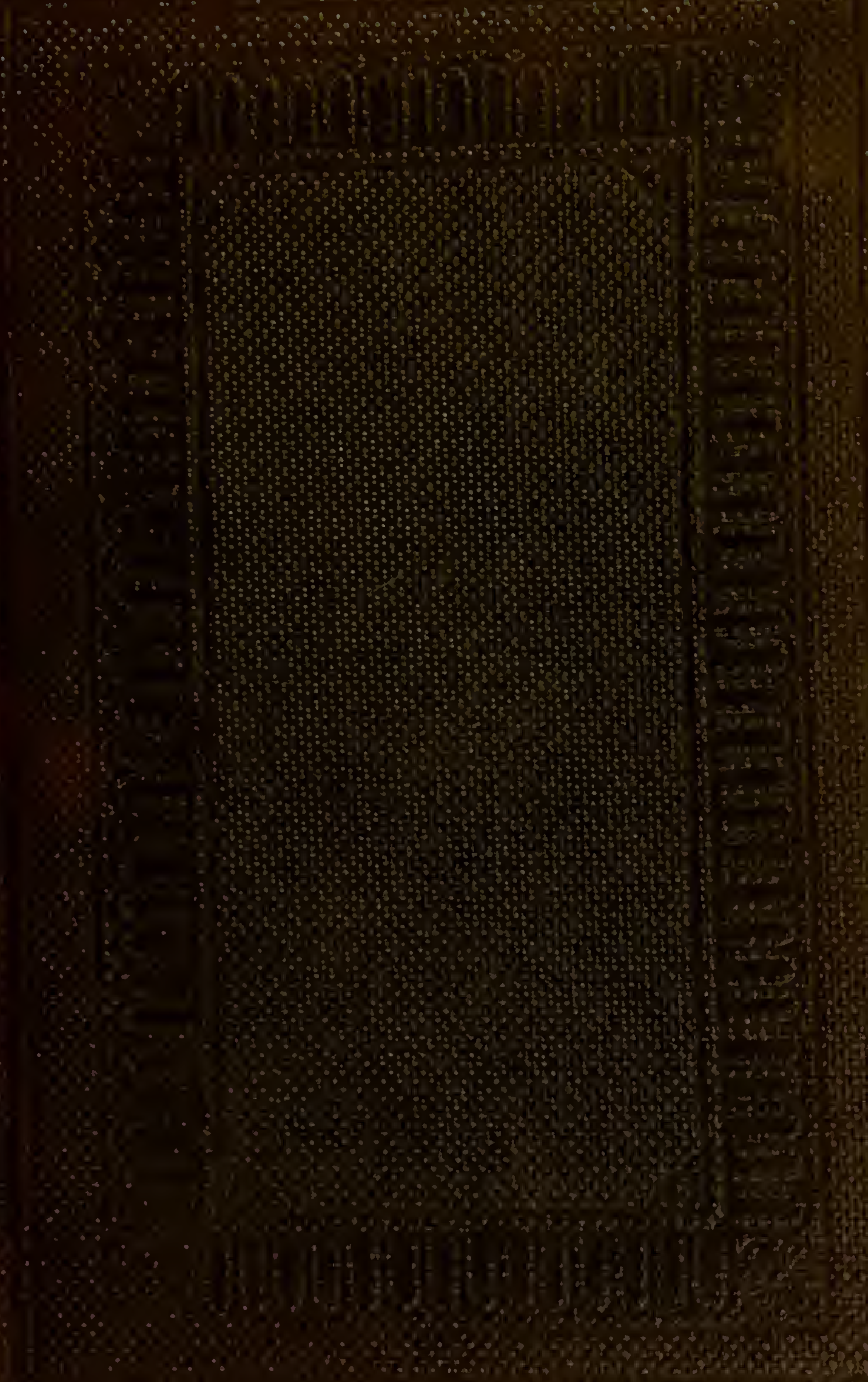

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A

HANDBOOK

OF

CHEMICAL ANALYSIS

(ADAPTED TO THE UNITARY NOTATION)

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A
HANDBOOK
OF
CHEMICAL ANALYSIS

(ADAPTED TO THE UNITARY NOTATION)

BASED ON THE FOURTH EDITION OF

DR. H. WILL'S

ANLEITUNG ZUR CHEMISCHEN ANALYSE.

BY

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PREFACE.

THE main object of this work is to further the general adoption in chemical instruction of the Unitary System of notation, by furnishing the laboratory student with a manual of analysis, in which this notation is adopted throughout. This system, first proposed by Gerhardt some sixteen years ago, and consistently advocated by Laurent, Williamson, Brodie, and other eminent chemists, has been gradually but surely gaining ground: until, at the present time, the only obstacle to its almost universal adoption in chemical schools is the want of books in which this system of notation is employed. This want will be supplied in the theoretical and descriptive branches of the science by the forthcoming Handbook of Chemistry by Dr. Odling: the present manual is designed to supply the same want in the analytical branch. I may add that the work was undertaken with Dr. Odling's knowledge and concurrence: and, in order to ensure uniformity between the two books on all essential points, the greater part of these sheets has been submitted to his inspection.

Independently, however, of the main object with which this work has been executed, I believe that there is room in English chemical literature for a text-book which aims at comprising the best and latest methods of analysis within a moderate compass. In German chemical literature this place is filled by the last edition of Dr. H. Will's *Anleitung zur*

Chemischen Analyse; a work which, beyond any other with which I am acquainted, combines the qualities of completeness and compactness. Those who are familiar only with the first edition of this book which was published in England some twelve years ago, can form no idea of the comprehensiveness and eminent practical utility of the later edition. Convinced that it was impossible to select a better model for a manual of analysis, I lost no time in communicating my design to Dr. Will, and soliciting his consent to its being carried out. This consent he at once granted: and I take this opportunity of acknowledging how fully his work is the foundation of mine. In fact, my first idea was simply to translate his book, merely making such alterations as were necessitated by the adoption of the new system of notation. But I found it advisable to make so many changes, both in the way of general arrangement, and of the introduction of fresh matter, that I abandoned this design, and resolved to take his book rather as a basis than as a strict model. These changes have been made principally in the two first parts of the work: in the remaining parts Dr. Will's book has been more closely adhered to, although in these also a considerable amount of fresh matter has been introduced. The Analytical Tables, especially, are little more than translations of those which accompany Dr. Will's manual. The last table, however, which gives the behaviour with acids of the majority of silicates, is entirely new: it has been compiled with great care from the works of Rammelsberg, Naumann, Brooke and Miller, Dana, and other authorities on mineralogy, in the belief that it will be found of service to students engaged in silicate analysis. In short, my object has been to produce a book which, while it possesses all the advantages of that on which it is based, presents the additional one of incorporating the best methods of analysis which have been introduced since the appearance of Dr. Will's work.

It would be out of place, in a purely practical manual, to enter into any explanation of the differences, or discussion of the respective claims, of the old system of notation and of that employed in this book. I shall confine myself to a simple statement of the changes which have been rendered necessary by the adoption of the new system. These consist mainly in doubling the atomic weights of ten of the elementary bodies, viz., oxygen, sulphur, selenium, tellurium, carbon, boron, silicon, tantalum, titanium, and tin. A corresponding change in the formulæ of all compounds in which any of these ten elements is combined with any of the remaining elementary bodies, follows as a necessary consequence; either the coefficient of the latter is doubled, or that of the former is halved. Thus *water* and *nitric acid*, which, under the old system, are expressed by the formulæ HO and NO^5,HO, respectively, become, in the new system, H^2O and NO^3H. Further, the adoption of that view of the constitution of salts, which regards them as acids in which the hydrogen is wholly or partially replaced by another metal, instead of that which represents them as compounds of an anhydrous acid with a metallic oxide, induces a change in the arrangement of the symbols by which these bodies are expressed. Thus, *nitrate of silver* is written NO^3Ag, not NO^5,AgO.

As this book is designed solely as a laboratory companion, and in no way aims at superseding the necessity of a teacher, I have not introduced into it any of that detail which belongs properly to works intended for self-instruction. Description of apparatus, directions for the preparation of reagents, &c., have been generally excluded: these are points on which the student will learn far more by a few days' practice in the laboratory than could be taught him by pages of written instruction. Besides, books already exist in which these and similar points are fully treated: and it has been my object throughout to keep the bulk of this volume within the narrowest possible limits. I have, however, thought it well to follow Dr. Will's example in not confining the work to qualitative analysis only. In the section which treats of quantitative analysis by weight, I have derived great assistance from Wöhler's *Handbook of Inorganic Analysis.* In the almost total absence of any English work on that branch of analysis, I hope that the few pages devoted to the very important subject of Volumetric Analysis will be found especially useful.

With a view of directing the student's attention in the first instance only to those elements which there is a reasonable chance of his meeting with in the ordinary course of analysis, I have printed in small type the sections relating to those elements which are of comparatively rare occurrence. I should recommend the beginner to confine his attention exclusively to that portion of the book which is printed in large type. It is of no use for him to burden his memory with the reactions of the rarer elements, until he is at least tolerably familiar with those of the bodies which he is likely to meet with at the commencement of his analytical practice.

In conclusion, I wish to record my acknowledgments to my friend Mr. G. C. Foster, of University College, to whose cooperation I have been indebted for most valuable assistance during the whole of the preparation of the book.

F. T. CONINGTON.

LONDON: December, 1858.

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HANDBOOK

OF

CHEMICAL ANALYSIS.

INTRODUCTION.

The object of Chemical Analysis is to ascertain the composition of any substance whatever. In doing this we may either rest contented with determining the elements of which it is composed, without paying any attention to their several quantities : or we may go further, and ascertain the exact proportion of each element which enters into its composition. Hence arises the distinction between *Qualitative* and *Quantitative* Analysis. Qualitative analysis teaches us how to ascertain the elements of a substance with regard to their quality only, and how to separate them from one another ; quantitative analysis establishes the methods of proceeding, by which we determine the relations of weight or volume which these elements bear to one another. It is obvious that, before we can proceed to estimate the quantities of each element contained in a compound, we must know what are the elements that it contains ; hence Qualitative must always precede Quantitative analysis.

The method of qualitative analysis consists in bringing the substance under examination into contact with other bodies of known properties, and observing the phenomena which ensue. These phenomena consist in alterations, either in state of aggregation, form, or colour, depending upon some chemical change. All bodies, which we employ for this purpose, we call by the general name of *reagents:* the ensuing phenomena we designate *reactions.* Acids, bases, salts, and simple bodies (elements), are alike used as reagents.

By means of reagents the chemist puts questions to the substance under examination, inquiring whether it contains this or that group of similar elements, or only this or that member of such groups. The answers to these questions are afforded by the occurrence or non-occurrence of the consequent reactions. If the question be put correctly, *i.e.* if all the conditions under which the reaction expected can be produced by the reagent employed be carefully observed, the answer is decisive as to the presence or absence of the element, or group of elements, sought; if, on the other hand, these conditions, *i. e.* the properties and chemical relations of the bodies formed by the chemical changes which constitute the reaction, have been wholly or partially neglected, the answer, if not certainly erroneous, is at least doubtful.

Reagents may be employed either in *the wet way* or in *the dry way.* In the wet way, the reagent in solution, *i. e.* in the liquid form, is brought into contact with the substance to be examined, which is also in the liquid form. In the dry way, the two bodies are brought together in the solid state, and subjected to a high temperature. Of the utmost importance in analysis by the latter method, is the knowledge of the use of the blow-pipe, and of the behaviour of bodies in the different flames which can be produced by this invaluable instrument. Whether he employ the wet or the dry way, the phenomena to be observed by the analyst are the same, consisting of indications either of oxidation, reduction, or double decomposition.

Many reagents exhibit the same or a similar behaviour with a certain fixed number, *i.e.* with a group, of elements, and with all the compounds of these elements; and can therefore be employed for the division of the elements into groups. Such reagents are termed *general reagents.* Others serve for the further distinction of the several members of such groups; their selection depends upon the knowledge of the special characteristic behaviour to such reagents of each single element, or of each of its several compounds. Such reagents are called *special* or *characteristic reagents.* Their number is much greater than that of the general reagents, their nature being as various as that of the substances which can come under examination; their selection depends upon the solubility or insolubility, colour, or other physical or chemical properties of the new compounds to which they give rise. They may frequently be employed reciprocally: thus, iodine is a characteristic reagent for starch, and reciprocally starch is a characteristic reagent for iodine.

The analyst has not only to establish that this or that body is present in a compound, but he has also to prove that no other body is present besides those that he has actually found. Hence it is evident that he must not treat the substance he is examining with any reagent indiscriminately. He must follow a certain fixed order, a methodical system, in the application of reagents, which will be the same for all inorganic substances whatever, let their elements be what they may. This systematic method, which cannot be departed from or abbreviated without danger, except in certain cases by the experienced chemist, consists, as is best shown in Table IV., in the employment of general reagents for the successive elimination of groups of elements possessing certain common chemical properties; and finally, in the recognition of each member of such groups by the employment of characteristic reagents. If the object be not a complete and accurate analysis, but merely to establish the presence or absence of some particular body, the characteristic reagent may in many cases be employed at once, without having previously had recourse to general reagents.

The foregoing remarks will enable the student to comprehend the system of arrangement which has been adopted in this work. Part I. contains a list of the most important reactions exhibited by the non-metallic elements and their compounds, when brought into contact, whether in the wet or dry way, with various reagents, both general and characteristic. In this class of bodies by far the greater number of acids are included. Part II. contains a similar enumeration of the reactions of the metals and their compounds. In this class are comprised by far the larger proportion of all known elements. They are divided into certain groups, according to their behaviour with a small number of general reagents, which have been selected by universal experience as affording the most convenient and best defined classification. Part III., to which the Tables belong, furnishes a complete systematic course of inorganic analysis, by pointing out the order in which the reagents mentioned in the two first parts may be most advantageously applied for the detection and separation of any inorganic body whatever. To it are added a few general remarks and cautions, intended at once to facilitate the course of analysis, and to render its results reliable. Part IV. is devoted to quantitative analysis; and Part V. to the best methods for the detection of the poisons of most frequent occurrence in judicial investigations.

PART I.

REACTIONS OF THE NON-METALLIC ELEMENTS AND THEIR MOST IMPORTANT COMPOUNDS.

This class of bodies comprises by far the greater number of those substances which possess an acid reaction[*], and which are therefore designated by the generic name of Acids. In this part, therefore, will be found the reactions by which the great majority of acids are distinguished. But, as there are some compounds of the non-metallic elements which are not acids, so there are some acids which contain metallic elements. Since, however, the characteristic reactions of these metallic acids depend upon the presence of the metallic element, they will naturally be treated of in Part II., which is devoted to metals and their compounds.[†]

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[*] The general reagent by which the presence of any acid is detected, is infusion of litmus, the blue colour of which is instantaneously changed to red on contact with an acid. It is this property of reddening litmus which is signified when a substance is said to have an *acid reaction*. Conversely, a body which possesses the property of restoring the blue colour of reddened litmus, is said to have an *alkaline reaction*. Another general test for such acids as are soluble in water, is their behaviour with carbonates, with which they cause effervescence, owing to the formation and decomposition of carbonic acid.

[†] As the sense in which we employ the term *acid* is somewhat different from that which is prevalent in most works on chemistry, it may be well to dwell briefly on the signification that we attach to it. We adopt the definition given by Gerhardt (Introduction à l'Étude de la Chimie, p. 103): *an acid is a salt whose base consists entirely of hydrogen*. Thus, nitric acid, NO^3H, is nitrate of hydrogen, just as NO^3Ag is nitrate of silver. In our view, therefore, the presence of basic hydrogen — *i. e.* of hydrogen which can be replaced by any other metal — is essential to the idea of an acid. Hence we hold that these bodies, which are commonly called *anhydrous acids*, are not acids at all; and, in fact they do not exhibit acid reactions. We propose to designate these bodies by the name *anhydrides* (*e.g.* sulphuric anhydride, SO^3; carbonic anhydride, CO^2, &c.).

The number of atoms of basic hydrogen varies in different acids, and on this

In this and the following Part, the letter (c) is attached to those reactions which are most characteristic, and on which the student should especially rely. The reactions not so marked may usefully be employed as confirmatory tests.

1. **Oxygen.** O. Atomic weight, 16.

A constituent of atmospheric air, of water, and of the majority of chemical compounds. A permanent gas, destitute of colour or smell. It is most easily recognised by its property of rekindling a glowing match that is introduced into it. (c) With nitric oxide it forms red fumes. (c) When mixed with twice its volume of hydrogen and ignited, combination takes place with explosion, and water is formed, no gaseous residue being left. It is but very slightly soluble in water. It is readily absorbed by the following reagents: (c) *phosphorus;* metallic *copper*, when heated to redness, or moistened with dilute sulphuric acid; a solution of *subchloride of copper* in ammonia; (c) a solution of *pyrogallic acid* in caustic potash, with which it gives a dark brown colour;

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variation is founded the distinction between *monobasic* and *polybasic* acids. A *monobasic* acid contains only 1 atom of basic hydrogen: in forming other metallic salts, therefore, it must always exchange the whole of its hydrogen for another metal, and so can only form *normal* salts; *e. g.* nitric acid, NO^3H; normal nitrate, NO^3K. A *bibasic* acid contains 2 atoms of basic hydrogen, one or both of which can be replaced by another metal. Besides the normal salt, therefore, in which both atoms of basic hydrogen are replaced by a metal, it can form one acid salt, in which only 1 atom is so replaced; *e. g.* sulphuric acid, SO^4H^2; normal sulphate, SO^4K^2; acid sulphate, SO^4KH. A *tribasic* acid contains 3 atoms of basic hydrogen, each of which can be separately replaced by another metal; and hence it can form, besides its normal salt, two acid salts, according as 1 or 2 of its atoms of basic hydrogen are so replaced; *e. g.* phosphoric acid, PO^4H^3; normal phosphate, PO^4K^3; monacid phosphate, PO^4K^2H; biacid phosphate, PO^4KH^2.

The term *neutral salt* is commonly applied to denote those salts in which the basic hydrogen of the acid is completely replaced by another metal, the name being founded on the presumption that such salts are without action on litmus. Since, however, this is far from being universally the case, it is better to designate such salts by the term *normal salts.*

In writing the formulæ of acids, we shall generally place the basic atom or atoms at the end of the formula. In this manner the basicity of an acid is rendered evident at a glance.

by *protohydrate of iron*, suspended in an alkaline liquid; by *alkaline sulphides;* and less rapidly by agitation with finely divided and moistened metallic *lead.* These and similar reagents for the absorption of gases, are principally employed in Eudiometry.

2. **Nitrogen.** N. Atomic weight, 14.

A constituent of the atmosphere. A permanent colourless gas, in which burning bodies are immediately extinguished. It is absorbed readily by boron, silicon, and titanium at high temperatures, the nitrides of these metals being formed. In order to detect nitrogen in any organic compound, the substance is dried and heated with caustic potash, when, if nitrogen be present, *ammonia* is evolved, and may be recognised by its smell, and by its forming white clouds on contact with a glass rod moistened with hydrochloric acid; or the substance is heated in a test-tube with a fragment of potassium, then dissolved in water, and tested for *cyanogen* with a proto- and sesqui-salt of iron and hydrochloric acid, or with sulphide of ammonium and sesquichloride of iron. (*See* Cyanogen, p. 41.)

Oxides and Acids of Nitrogen. a. *Nitric Acid*, NO^3H.— Pure nitric acid is a colourless corrosive volatile liquid; when it contains nitrous acid, it is of a deep yellow colour. It readily parts with half its oxygen, generally giving off nitric oxide, NO, which forms red fumes on contact with the air. It is a powerful oxidising agent, attacking all metals except platinum, iridium, rhodium, and gold; converting most lower metallic oxides into higher oxides; and oxidising all sulphides (except sulphide of mercury) into the corresponding sulphates, generally with separation of sulphur, which by prolonged digestion is converted into sulphuric acid. It forms soluble salts with all metals: hence it precipitates no metal, nor is there any reagent by which it can be precipitated. Tin, antimony, tungsten, and tellurium are the only metals which, when treated with nitric acid, form oxides insoluble in the acid; the sulphate of lead, which is formed by treating sulphide of lead with nitric acid, is similarly insoluble. Most nitrates are less soluble in nitric acid than in water. Insoluble basic nitrates are readily soluble in dilute sulphuric or other mineral acids.

Nitric acid and other nitrates are decomposed when heated with concentrated hydrochloric acid, or other chlorides, chlorine being evolved ; this mixture (*aqua-regia*) readily dissolves gold-leaf, and decolorises solution of indigo. (c) When a solution of a nitrate is mixed with about its own volume of pure concentrated sulphuric acid, the mixture allowed to cool, and a few drops of a concentrated solution of *protosulphate of iron* gently poured upon it, a ring is formed at the point of contact of the two liquids of a violet, amethyst, red, or dark brown colour, according to the quantity of nitrate present. The coloration is increased by the careful agitation of the mixture, and disappears on the application of heat. In the absence of chlorine compounds the smallest trace of a nitrate may be detected by this test. Very dilute solutions, (as mineral-water, rain-water, or water issuing from the soil,) require concentration before applying this reaction. When a solution of a nitrate is heated with sulphuric acid and a drop of solution of indigo, the blue colour of the indigo is changed to yellow : this reaction is rendered more delicate by the addition of a little chloride of sodium. When a dry and pure nitrate is heated with concentrated sulphuric acid, colourless vapours of nitric acid are evolved, which form white clouds on contact with ammonia, and do not precipitate a silver solution. (c) If *metallic copper* or *protosulphate of iron* be added to the mixture, red nitrous fumes are evolved, and, if a chlorine compound be present, free chlorine also. If the quantity of nitrate present be very minute, the nitrous fumes may not be visible to the eye, but they may be detected by leading the gas evolved into a solution of starch and iodide of potassium, when, if the least trace of nitrous fumes be present, the characteristic purple colour of iodide of starch will be produced. The same reaction is effected in the dry way by fusing a nitrate with acid sulphate of potassium. All nitrates, when fused with potash and any non-nitrogenised organic body, as sugar, evolve ammonia. When heated with an excess of *protochloride of iron* and hydrochloric acid, all nitrates give off nitric oxide, which, when mixed with sulphuretted hydrogen, and led (in an atmosphere of hydrogen) over heated soda-lime, is entirely converted into ammonia. The ammonia is easily estimated by leading it into a standard solution of sulphuric acid. This is often a convenient method for the estimation of nitric acid.

All nitrates are decomposed at a high temperature ; nitrate of ammonium entirely into nitrous oxide and water ($NO^3NH^4 = N^2O + 2H^2O$). The decomposition by heat of all other nitrates varies with the nature of the base, but generally they are all decomposed into oxygen and some lower oxide of nitrogen. When heated with charcoal, or especially with cyanide of potassium, sulphur, or phosphorus, nitrates explode violently.

Estimation of Nitric Acid.—This is usually effected by saturating the acid with excess of carbonate of barium, heating the mixture in order to decompose any acid carbonate, filtering off and thoroughly washing the excess of carbonate, and precipitating by sulphuric acid the barium contained as nitrate in the filtrate. This process can only be applied directly when the nitric acid is free, and no other acid is present. In the analysis of a nitrate, the nitric acid is liberated by distillation with sulphuric acid ; the distillate is treated as above. The same distillation separates nitric acid from any non-volatile acids that may be present ; if other volatile acids are present they must be removed before distilling.

Nitric acid may also be estimated volumetrically (*see* Part IV.) by means of a standard solution of chloride of tin in hydrochloric acid. A known volume of the tin-solution, more than can be completely converted into perchloride by the nitric acid employed, is heated, together with the nitric acid (or nitrate) in a sealed tube, to about 150° for ten minutes. The contents of the tube are then transferred to a beaker, a little iodide of potassium and starch added, and the remaining chloride of tin estimated by a standard solution of bichromate of potassium. Each atom of nitric acid converts 4 atoms chloride of tin into perchloride ($NO^3H + 4SnCl^2 + 8ClH = 4SnCl^4 + NH^3 + 3H^2O$).—Pugh.

b. *Peroxide of Nitrogen* (hyponitric acid), NO^2. *Nitrous Anhydride*, N^2O^3.—Yellowish or reddish-brown gases, formed by the contact of nitric oxide with oxygen, and by the decomposition by heat of most nitrates. On contact with water they are decolorised and decomposed; NO^2 into nitric and nitrous acids ($2NO^2 + H^2O = NO^3H + NO^2H$); and N^2O^3 into nitric acid and nitric oxide ($3N^2O^3 + H^2O = 2NO^3H + 4NO$). At a very low temperature they are condensed, the former to a brown, the latter to a bluish-green liquid. Both are constituents of the red fuming nitric acid.

c. *Nitrous Acid*, NO^2H.—Formed, as we have seen, by the decomposition of NO^2 in contact with water. It can never be obtained free from nitric acid, for its solution is always partially decomposed into nitric acid and nitric oxide ($3NO^2H = NO^3H + 2NO + H^2O$). All nitrites are soluble in water.

Aqueous solutions of alkaline nitrites are decomposed by *hydrosulphuric acid*, sulphides of the alkaline metals being formed; in acid solutions the decomposition is accompanied by a separation of sulphur. When treated with dilute sulphuric or nitric acid, nitrites give off red fumes; on the addition of the same acids, they decolorise *permanganate of potassium*, and gradually change the colour of *bichromate of potassium* to a greenish blue. (c) Free nitrous acid at once produces a purple colour with starch and iodide of potassium. Since pure nitric acid exhibits none of these reactions, they serve to detect nitrous in presence of nitric acid. (c) All nitrites give a dark-brown colour with protosalts of iron, without the addition of acid. Pure nitrates do not exhibit this reaction; for the employment of this test for the detection of nitric acid (p. 8) depends upon the partial reduction of the nitric to nitrous acid. Nitrites reduce *terchloride of gold* and *subsalts of mercury*, giving with the former a brown precipitate of metallic gold, with the latter a grey precipitate of metallic mercury. Alkaline nitrites give a yellow precipitate with protosalts of *cobalt*, which forms slowly (p. 145). An aqueous solution of nitrite of ammonium, or of any nitrite on addition of chloride of ammonium, is decomposed by heat into nitrogen and water, ($NO^2NH^4 = N^2 + 2H^2O$). (c) *Urea* is decomposed by nitrous (not by nitric) acid, with evolution of carbonic anhydride and nitrogen ($CH^4N^2O + 2NO^2H = CO^2 + N^4 + 3H^2O$). Many nitrogenised organic compounds, *e. g.* protein, give a deep red colour when heated with a solution of mercury in nitric acid, containing some nitrite. (c) Both nitric and nitrous acids impart a deep yellow colour to all nitrogenised organic compounds; *e. g.* the human skin, feathers, &c.

d. *Nitric Oxide*, NO. — A colourless gas, which, on contact with oxygen forms red fumes of NO^2 and N^2O^3. (c) It is readily and completely absorbed by a solution of a *protosalt of iron*, giving a red or dark brown colour, and by concentrated *nitric acid*, giving a blue, green, or yellow colour. These reactions distinguish it from all known gases. The dark brown compound which it forms with protosalts of iron contains 4 atoms of the iron salt to 2 atoms of nitric oxide: it is on the formation of this body that the best test for the detection of nitric acid depends (p. 8). On contact with red-hot metallic copper, nitric oxide, like all other oxides of nitrogen, gives up its oxygen, free nitrogen being evolved.

e. *Nitrous Oxide* (laughing gas), N^2O.—A colourless gas, which is not coloured by contact with oxygen. It is somewhat soluble in water. Like oxygen, it rekindles a glowing match, but it is readily distinguished from oxygen by its remaining colourless on contact with nitric oxide. Heated potassium deprives both nitrous and nitric oxide of all their oxygen ; in the former case the original volume of the gas remains unaltered, in the latter it is diminished one half.

3. **Carbon.** C. Atomic weight, 12.

One of the most widely spread of the elements. In the uncombined state it is found native in two modifications, differing most widely in their physical properties : the crystalline, as the diamond; and the amorphous, as graphite or blacklead, and anthracite. Amorphous carbon is always black. Only the amorphous modification can be prepared artificially ; *e. g.* soot, charcoal, &c. In combination with other elements carbon is of the most frequent occurrence in nature. It is a constituent of all organic bodies, without exception : as carbonic anhydride, it occurs in the atmosphere ; as carbonic acid, in all springs and mineral waters ; and, in many minerals, in combination with calcium, barium, magnesium, iron, and other metals. The characteristic properties of carbon are, its insolubility in acids or alkalis, its absolute resistance to the action of heat in a closed vessel, and its combustion to carbonic anhydride when heated in contact with oxygen. When fused with saltpetre, its combustion takes place with a violent explosion. Every carbon compound, when heated to redness with oxide of copper or chromate of lead, gives off carbonic anhydride, which may be recognised by means of lime-water or acetate of lead, and is completely absorbed by caustic potash.

OXIDES AND ACIDS OF CARBON. a. *Carbonic Anhydride*, CO^2.—A colourless condensible* gas, having a slightly pungent smell; considerably heavier than atmospheric air. It is somewhat soluble in water; the solution reddens litmus-paper, but not permanently; it gives off most of the dissolved anhydride on standing for a time, and the whole on the application of heat.

b. *Carbonic Acid*, CO^3H^2.—An aqueous solution of carbonic acid, gives with *lime-* or *baryta-water*, a white precipitate, soluble in excess of carbonic acid. These are the reactions generally employed for the detection of carbonic acid in mineral waters. *Acetate of lead* gives a white precipitate in very dilute solutions of carbonic acid. Carbonic acid is readily absorbed by caustic potash, whether in the solid state or in solution. The only normal carbonates that are soluble in water are those of the alkaline metals: their solution has an alkaline reaction, and gives precipitates with the salts of all other metals. Some normal carbonates (those of the metals of the alkaline earths, magnesium, iron, and manganese) are soluble in free carbonic acid, being converted into acid carbonates: on heating the solutions, a precipitate of a normal or basic salt is formed. With solutions of normal carbonates, salts of *calcium*, *barium*, *magnesium*, *lead*, and *silver* give a white, *chloride of mercury*, a brick-red, precipitate, even in very dilute solutions: all these precipitates are readily soluble in nitric or acetic acid. The normal carbonates of barium, strontium, calcium, and magnesium are all more or less soluble in chloride of ammonium, especially on heating: carbonate of magnesium is not reprecipitated from this solution by free ammonia. A solution of an acid carbonate gives no precipitate with *sulphate of magnesium:* with *chloride of mercury*, a gradual white precipitate. A very dilute solution of a *calcium*-salt is not precipitated by an alkaline acid carbonate. Salts of aluminium and sesquisalts of iron are precipitated by acid carbonate of sodium.

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* A gas is said to be *condensible* when it can be liquefied by pressure and cold. Gases which cannot be so liquefied are called *permanent*.

Solid carbonates, as well as their solutions, when not too dilute, are easily recognised by their being decomposed *with effervescence* by strong acids. (c) The gas evolved is almost destitute of smell, and gives a white precipitate when led into lime-water or acetate of lead. Other salts, as sulphites and sulphides, are similarly decomposed with effervescence by acids: but the gases evolved in these cases have a peculiar and characteristic smell. Cyanates also evolve carbonic anhydride when treated with acids; but the gas in this case is always accompanied by the penetrating smell of cyanic acid, and the residue contains an ammonium-salt. Some native carbonates (*e. g.* spathic iron-ore and dolomite) are not thus decomposed by acids without the application of heat.

The normal carbonates of potassium and sodium are not decomposed by the strongest heat. The carbonates of barium and strontium require the strongest white heat for their decomposition, and the carbonate of calcium a strong red heat. These carbonates are decomposed at a much lower temperature if any free carbon or organic matter be present, carbonic oxide being formed. All other carbonates are easily decomposed by heat, carbonic anhydride being evolved, and metallic oxides left.

Estimation of Carbonic Acid.—Carbonic acid is estimated in solid carbonates, by the loss of weight which they undergo when decomposed by a not too dilute acid, in an apparatus which admits of accurate weighing, and ensures the perfect drying of the carbonic anhydride evolved (p. 233). The carbonic acid dissolved in mineral waters is estimated by precipitating it by a mixture of chloride of calcium and ammonia, and weighing the resulting carbonate; or volumetrically by means of solution of litmus, and a standard solution of an alkali. From a gaseous mixture of carbonic anhydride with sulphurous anhydride and sulphuretted hydrogen, the two latter may be entirely removed by means of peroxide of lead, peroxide of manganese, or oxide of mercury; these substances may be taken up moist on the end of a glass rod or a platinum wire, dried, and introduced into the gaseous mixture. Or the sulphurous anhydride may be removed by a concentrated solution of bichromate of potassium mixed with sulphuric acid; and the sulphuretted hydrogen by sulphate of copper. Carbonic anhydride is easily separated from most remaining gases by means of caustic potash, by which it is completely absorbed.

c. *Carbonic Oxide*, CO.—Formed by the imperfect oxidation of carbon, or the deoxidation of carbonic anhydride. A colourless gas, burning with a blue flame. It is absorbed by fused *potassium*, by a solution of *subchloride of copper* in ammonia, or by *subsulphite of copper*. 2 volumes of carbonic oxide exploded with 1 volume of oxygen, form 2 volumes of carbonic anhydride.

HYDRIDES OF CARBON. HYDROCARBONS. — These compounds, which are very numerous, properly belong to organic chemistry. There are, however, two of them which are frequently met with in gaseous mixtures, with the properties of which the student must early be acquainted, for which reason they are mentioned here.

a. *Olefiant Gas*, C^2H^4.—A colourless gas, which burns with a very brilliant flame. It is entirely absorbed by fuming sulphuric acid. When mixed with an equal volume of chlorine, combination takes place, even in the dark, an oily liquid being formed, $C^2H^4Cl^2$.

b. *Marsh Gas* (light carburetted hydrogen), CH^4. — A colourless gas, burning with a feeble blue flame. It is not absorbed by fuming sulphuric acid. In presence of water it does not combine with chlorine in the dark; but the access of light determines the combination, carbonic anhydride being formed. 1 volume of marsh gas exploded with 2 volumes of oxygen forms water, and 1 volume carbonic anhydride.

Of the vast number of acids containing carbon, which are included under the general name of *organic acids*, only a few are of sufficient importance as reagents, to call for mention in a work on analysis. They would naturally come under this section, but as it is well that the student should first become familiar with the common mineral acids, the reactions of the more important organic acids will not be treated of till the close of this part.

4. **Sulphur.** S. Atomic weight, 32.

Sulphur is found in nature both free and combined: in the former state it is commonly a volcanic product, and is frequently crystalline; in the latter, it occurs as hydrosulphuric acid in mineral waters; in combination with metals, as metallic sulphides (pyrites, galena, cinnabar, &c.); and combined with metals and oxygen, as metallic sulphates.

ACIDS AND OXIDES OF SULPHUR. a. *Hydrosulphuric Acid* (sulphuretted hydrogen), SH^2. *Metallic Sulphides.*—Hydrosulphuric acid is a colourless condensible gas, possessing a characteristic smell, resembling that of rotten eggs; it burns with a blue flame. Cold water absorbs about three times its volume of the gas, the solution (sulphuretted hydrogen water) is gradually decomposed by contact with the air, losing its smell and depositing sulphur ($SH^2+O=OH^2+S$). Both the gas and the solution redden litmus feebly. With most metallic oxides, hydrosulphuric acid (both in the wet and dry way) forms water and metallic sulphides: the latter have very frequently a characteristic colour ($SH^2+OM^2=SM^2+OH^2$).

The compounds of sulphur with the alkaline and alkaline-earthy metals, are soluble in water; those with the heavy metals are insoluble. Some few sulphides part with their sulphur when heated in a closed vessel (sulphides of gold and platinum): some higher sulphides (bisulphide of iron, pentasulphide of antimony) part with a portion of their sulphur. All sulphides, when heated in the air, give off sulphurous anhydride; the residue in some cases is the metal (silver); in others, a metallic oxide (tin, antimony, bismuth, molybdenum); in others, a metallic sulphate (the alkaline and alkaline-earthy metals, copper, lead, &c.). Some metallic sulphides are soluble in dilute hydrochloric acid with evolution of hydrosulphuric acid (sulphides of the alkaline and alkaline-earthy metals, iron, manganese, zinc, uranium); others require concentrated hydrochloric acid for their solution (sulphides of nickel, cobalt, antimony, lead); others are insoluble even in concentrated hydrochloric acid (sulphides of arsenic, copper, mercury, gold, platinum, &c.). All sulphides (except sulphide of mercury) are decomposed by digestion with concentrated nitric acid, aqua-regia, or hydrochloric acid and chlorate of potassium, with formation of sulphuric acid, and a metallic oxide or chloride, and, in case the acid be not sufficiently concentrated or the digestion not continued long enough, separation of sulphur. Sulphide of mercury is not decomposed by pure nitric acid, but readily by aqua-regia; sulphide of lead is converted by nitric acid into sulphate of lead, sulphide of tin into binoxide of tin, sulphide of antimony into antimonic oxide or anhydride (*see* p. 7, Nitric Acid). When heated in a current of chlorine, all sulphides are converted into metallic chlorides and chloride of sulphur.

The sulphides soluble in water are distinguished into *proto-* or *mono-sulphides* (K^2S, $(NH^4)^2S$, Ba^2S), *hydrosulphates* (KHS, NH^4HS,) and *polysulphides* (K^2S^5, $(NH^4)^2S^5$). The aqueous solution of the two first is colourless, and when treated with acids gives off hydrosulphuric acid without any separation of sulphur; that of the last is yellow, or yellowish-brown, and when treated with acids gives off hydrosulphuric acid, and deposits sulphur. With *protosulphate of manganese*, soluble monosulphides give a precipitate of sulphide of manganese, without evolution of hydrosulphuric acid; hydrosulphates with the same reagent evolve hydrosulphuric acid ($SO^4Mn^2 + 2SKH = SO^4K^2 + SMn^2 + SH^2$). All soluble sulphides (and some of them which are insoluble) rapidly absorb oxygen from the air, and are decomposed. The decomposition goes through several stages; a polysulphide is first formed, then a hyposulphite, and finally, in most cases, a sulphite and a sulphate.

(c) The presence of hydrosulphuric acid, or of a soluble sulphide, is at once detected, either in a neutral, acid, or alkaline solution, by the black precipitate of sulphide of lead which it gives with any *lead*-salt: if the smallest trace of hydrosulphuric acid be present in a gaseous mixture, a piece of paper moistened with acetate of lead, and exposed to the gas, is covered with a black or dark-brown shining film of sulphide of lead. Hydrosulphuric acid is entirely absorbed by a solution of potash or ammonia.

(c) *Nitroprusside of Sodium* produces no change of colour in sulphuretted hydrogen water, or in any acid solution containing hydrosulphuric acid: but if the smallest trace of a soluble sulphide be present, this reagent gives, even in presence of free hydrosulphuric acid, a magnificent purple colour, which disappears after some time. This is the best test for determining whether a solution contains a soluble sulphide, as well as free hydrosulphuric acid. The coloration is not immediately destroyed even by very great dilution.

Estimation of Hydrosulphuric Acid.—An alcoholic solution of iodine, or better, an aqueous solution of iodine in iodide of potassium, immediately decomposes hydrosulphuric acid with formation of hydriodic acid and sulphur, which latter causes a milkiness in the solution ($I^2 + SH^2 = 2\,IH + S$). If an iodine solution of known strength be employed, and a little starch added to the solution under examination, the appearance of a blue colour indicates with certainty the exact point at which all the hydrosulphuric acid is decomposed: and the amount of that acid present may be calculated from the quantity of iodine solution used. Soluble sulphides behave with iodine exactly like hydrosulphuric acid. If the solution be alkaline, it must be neutralised with acetic acid before adding the iodine solution. Hydrosulphuric acid is also decomposed by *chlorine*, *bromine*, *sulphurous*, *hypochlorous*, *nitrous*, *iodic*, and *chromic acids*, and *sesquisalts of iron*, sulphur being separated, and generally a sulphate formed.

The general method of estimating the sulphur in metallic sulphides is to oxidise it completely by digestion with aqua-regia, or fuming nitric acid, and to precipitate the sulphuric acid formed by chloride of barium (p. 211).

Blowpipe reactions (*see* p. 24).

b. *Sulphuric Anhydride*, SO^3.—A white crystalline feathery solid, resembling asbestos in appearance; giving off white suffocating fumes on contact with the air. It is very readily soluble in water with great evolution of heat. Combined with one atom of water it forms

c. *Sulphuric Acid*, SO^4H^2.—An oily colourless heavy liquid, powerfully corrosive, boiling at 327°. It is soluble in water in all proportions: the combination is attended with great heat. It is so hygroscopic (*i. e.* has so strong a tendency to take up water) that it is employed to dry substances which will not bear an elevation of temperature. It is the most powerful acid with which we are acquainted, and in the wet way will displace all other acids from their salts. It is bibasic; and therefore forms acid as well as normal salts (p. 6).

All normal and acid sulphates (with the few following exceptions) are soluble in water: basic sulphates are insoluble in water, soluble in dilute acids. Sulphate of barium is entirely insoluble in water or dilute acids: sulphate of calcium is difficultly soluble in water (in 500 parts); sulphate of strontium still less soluble (in 9000 parts); and sulphate of lead still less (in 22,000 parts). (C) The best reagent for the detection and estimation of sulphuric acid in solutions is *chloride*, or *nitrate of barium*, either of which gives a white, finely divided precipitate of sulphate of barium (SO^4Ba^2), which is very slightly soluble in concentrated nitric or hydrochloric acids. The solution of the sulphate should first be acidulated with hydrochloric acid. Care must be taken not to have too much free nitric or hydrochloric acid present; for, as chloride and nitrate of barium are much less soluble in strong acids than they are in water, their addition to a strongly acid solution might cause a precipitate, even if no sulphuric acid were present. When, therefore, either of these reagents causes a precipitate, excess of water should be added, which will at once dissolve any chloride or nitrate of barium that may be precipitated, but will not dissolve the sulphate. If the amount of sulphate present be very minute, the solution (especially if it contains nitric acid) should be allowed to stand some time after the addition of the barium-salt. If sulphate of barium be precipitated from a solution containing a nitrate, it generally carries down with it some nitrate of barium, which cannot be entirely removed by washing with water. In such cases, therefore, in quantitative analysis, the precipitate must be ignited (in order to decompose the nitrate), moistened with hydrochloric acid, and washed till it is quite free from chloride of barium. Freshly precipitated sulphate of barium is very apt to pass through the filter: this may generally be obviated by heating the solution with the precipitate some time before filtering. This reaction distinguishes sulphuric acid from all other acids, except selenic and fluosilicic acids, which also form barium-salts insoluble in water and dilute acids. Sulphate of barium is however easily distinguished from selenate and fluosilicate by the following reactions. Selenate of barium is decomposed when heated with concentrated hydrochloric acid, chlorine being evolved and selenous acid formed; also by ignition in a current of hydrogen, selenide of barium being formed, which is readily soluble in hydrochloric acid. Fluosilicate of barium, when heated with strong sulphuric acid, evolves hydrofluoric acid, which is readily recognised by its corrosive action on glass. Sulphate of barium is not affected by any of these reagents.

Sulphates are mostly insoluble in alcohol: the addition of alcohol ensures the complete precipitation of calcium-, strontium-, and lead-salts by sulphuric acid. Sulphate of lead is less soluble in water containing sulphuric acid, than in pure water, requiring 36,500 parts of the former. The sulphates of the alkaline and alkaline-earthy metals and lead, are not decomposed by heat: all other sulphates are decomposed by heat, giving off sulphuric anhydride, or sulphurous anhydride and oxygen, according to the nature of the metal. All sulphates are decomposed when heated with charcoal; the sulphates of the alkaline and alkaline-earthy metals (and lead) being reduced to sulphides, and the other sulphates evolving sulphurous anhydride. Those sulphates which are insoluble in water and acids are entirely decomposed by fusion with an alkaline carbonate, ($SO^4 Ba^2 + CO^3 Na^2 = SO^4 Na^2 + CO^3 Ba^2$). The fused mass should be treated with hot water (not with acids), filtered, and the filtrate saturated with hydrochloric acid, when the addition of chloride of barium will show the presence of sulphuric acid. The sulphates of strontium and calcium are entirely decomposed by carbonate of ammonium in the cold: sulphate of barium is not attacked by it.

Blowpipe reactions (*see* p. 24).

d. *Sulphurous Anhydride*, SO^2. — The only product of the combustion of sulphur in the air. It is also formed by the ignition of metallic sulphides, by the deoxidation of sulphuric acid by charcoal, organic compounds, and several metals, &c. It is at the ordinary temperature a colourless gas, with a characteristic smell, which is familiar to every one as that caused by burning sulphur. It is readily soluble in water, forming

e. *Sulphurous Acid*, SO^3H^2 (bibasic). — Its solution is very unstable, giving off sulphurous anhydride even at the common temperature.

The only normal sulphites that are soluble in water, are those of the alkaline metals: those which are insoluble in water are readily soluble in sulphurous or hydrochloric acids. Solutions of sulphites when exposed to the air absorb oxygen, and are converted into sulphates. When heated with concentrated nitric acid, or treated with chlorine, hypochlorous acid, or iodine, they are immediately converted into sulphates without separation of sulphur. All sulphites, whether solid or in solution, when treated with a strong acid (sulphuric acid is best), evolve sulphurous anhydride, which is easily recognised by its smell: in the case of a solid sulphite, or a concentrated solution, the gas escapes with effervescence. In this reaction there is no separation of sulphur. (c) *Chloride of barium* gives with sulphites a white finely divided precipitate of sulphite of barium, insoluble in water, readily soluble in hydrochloric acid: on the addition to this solution of hypochlorite of sodium, chlorate of potassium, chlorine-water, or iodine, sulphate of barium is at once precipitated. This reaction distinguishes sulphurous from carbonic acid. *Acetate of lead* gives a white precipitate of sulphite of lead, readily soluble in dilute nitric acid. (c) *Nitrate of silver* gives a white precipitate of sulphite of silver, which blackens on heating, owing to the reduction of metallic silver; the solution then contains sulphuric acid. *Subnitrate of mercury* gives a grey precipitate of metallic mercury.

Sulphurous acid is a powerful reducing agent: it precipitates metallic gold from terchloride of gold, reduces chromic acid to green sesquioxide of chromium, arsenic acid by long digestion to arsenious acid, sesquisalts of iron to protosalts, tellurous and selenous acids to metallic tellurium and selenium, &c. Metallic zinc is dissolved by sulphurous acid without any evolution of gas, sulphite and hyposulphite of zinc being formed ($Zn^4 + 3SO^3H^2 = SO^3Zn^2 + S^2O^3Zn^2 + 3OH^2$): if hydrochloric acid be present, hydrosulphuric acid is evolved, and may be detected by paper moistened with acetate of lead. By this reaction the smallest traces of sulphurous acid may be detected (in hydrochloric acid, &c.). Most of the following sulphur-acids exhibit the same reaction. Aqueous sulphurous acid is decomposed by hydrosulphuric acid, pentathionic acid being formed and sulphur deposited ($5SH^2 + 5SO^3H^2 = S^5O^6H^2 + S^5 + 9OH^2$).

When a solution of sulphurous acid is heated with chloride of tin and hydrochloric acid, yellow sulphide of tin is gradually precipitated: this reaction is rendered more delicate by the addition of a drop of a soluble copper-salt, owing to the formation of black sulphide of copper. In this reaction a piece of paper moistened with acetate of lead should be held to the mouth of the tube, since the hydrosulphuric acid is frequently evolved in the free state. Sulphurous anhydride is readily and completely absorbed by peroxide of lead, sulphate of lead being formed ($Pb^2O^2 + SO^2 = SO^4Pb^2$). If a glass rod moistened with solution of starch and iodate of potassium be introduced into a gaseous mixture containing sulphurous anhydride, blue iodide of starch is at once formed.

Most sulphites are decomposed by heat into a sulphate and a sulphide ($4SO^3K^2 = 3SO^4K^2 + SK^2$): the earthy sulphites give off sulphurous anhydride, a metallic oxide being left.

Estimation of Sulphurous Acid.—Sulphurous acid is the only oxygen compound of sulphur which (completely in very dilute solutions not containing more than 0·04 p. c. of acid) is converted by iodine into sulphuric acid ($SO^3H^2 + H^2O + I^2 = SO^4H^2 + 2HI$). This reaction serves not only for the detection, but, by the use of a standard iodine solution, for the volumetric estimation of sulphurous acid.

Sulphurous acid may also be oxidised into sulphuric acid, and estimated as sulphate of barium.

Blowpipe reactions (*see* p. 24).

f. *Hyposulphurous Acid* (Dithionous acid), $S^2O^3H^2$.—Formed by the digestion of a sulphite with sulphur: by the oxidation of soluble sulphides in contact with the air: by dissolving sulphur in a solution of an alkaline hydrate, when a metallic sulphide is formed simultaneously. It is so unstable an acid that it cannot be obtained in the free state, for its aqueous solution is decomposed spontaneously (if dilute, slowly, if concentrated, immediately) into sulphurous acid and sulphur, the latter of which separates out ($S^2O^3H^2 = SO^3H^2 + S$).

Most hyposulphites are soluble in water: the barium-salt is difficultly soluble. Their solutions give with *proto-salts of mercury*, salts of *lead* and *silver*, white precipitates of metallic hyposulphites, which speedily become yellow, brown, and black, especially if heat be applied, owing to the decomposition of the hyposulphite and formation of a metallic sulphide, sulphuric acid remaining in solution ($S^2O^3Ag^2 + OH^2 = Ag^2S + SO^4H^2$). With *chloride of tin* they give a brown, with *subnitrate of mercury* a black, precipitate of metallic sulphide. Solutions of hyposulphites dissolve chloride of silver, subchloride of mercury, and sulphate of lead. (c) When heated with hydrochloric acid, hyposulphites evolve sulphurous anhydride and deposit sulphur, which in this case is yellow, not white, as it usually is when separated from solutions by chemical action. When treated with iodine they form a metallic iodide and a tetrathionate ($2S^2O^3Ba^2 + I^2 = S^4O^6Ba^2 + 2IBa$.) These two reactions distinguish hyposulphurous from sulphurous acid. When treated with hypochlorite of sodium, or chlorine, hyposulphites are completely oxidised into sulphates, even at the ordinary temperature ($S^2O^3Na^2 + Cl^8 + 5OH^2 = 2SO^4 NaH + 8ClH$). All hyposulphites are decomposed by heat: those of the alkaline metals into a polysulphide and a sulphate ($4S^2O^3 K^2 = S^5K^2 + 3SO^4K^2$): others into sulphides or sulphates, with evolution of sulphurous anhydride, owing to the combustion of separated sulphur. With zinc and hydrochloric acid hyposulphites behave like sulphites.

In order to detect hyposulphurous acid in presence of hydrosulphuric acid or a soluble sulphide, the solution is made neutral and precipitated by a zinc salt, the sulphide of zinc filtered off, and the filtrate tested for hyposulphurous acid.

Blowpipe reactions (*see* p. 24).

g. *Hyposulphuric Acid* (Dithionic acid), $S^2O^6H^2$.—Formed by the action of binoxide of manganese on an aqueous solution of sulphurous acid, a sulphate being always formed simultaneously ($2\,Mn^2O^2 + 3SO^3H^2 = S^2O^6Mn^2 + SO^4Mn^2 + 3OH^2$).

All hyposulphates are soluble in water; hence, their solutions are not precipitated by any reagents. When treated with hypochlorite of sodium *in the cold*, their solutions are not oxidised into sulphates; but when heated with nitric acid, or hydrochloric acid and chlorate of potassium, they are completely oxidised into sulphates. When heated with a non-oxidising mineral acid (sulphuric acid is best) they are decomposed, a sulphate being formed and sulphurous anhydride evolved, but no sulphur separated: with solid hyposulphates, concentrated sulphuric acid effects this decomposition in the cold. In the dry way, they are decomposed by heat in precisely the same manner.

Hyposulphuric acid is distinguished from sulphuric and sulphurous acids, by the solubility of its barium-salt; from hyposulphurous and the other polythionic acids, by its not separating sulphur when decomposed by acids, and by its giving no precipitate with salts of silver or mercury.

h. Besides those above enumerated, there are other acids formed by the combination of sulphur, oxygen, and hydrogen. They are *trithionic acid*, $S^3O^6H^2$; *tetrathionic acid*, $S^4O^6H^2$; and *pentathionic acid*, $S^5O^6H^2$. These acids resemble each other considerably in their reactions; but as they are very rare acids, that would never be met with in actual analysis, it is not necessary, in a practical work, to do more than indicate their existence. These acids, together with dithionous and dithionic acids, form the series called *polythionic acids*, *i. e.* acids containing more than one atom of sulphur.

All polythionates are decomposed when heated with cyanide of mercury, hydrocyanic acid being evolved. In the case of dithionites (hyposulphites), 1 atom of sulphide of mercury is formed to 1 atom of sulphuric acid; in the case of all the rest, 1 atom of metallic sulphide is formed to 2 atoms of sulphuric acid. With tetrathionates, 1 atom, with pentathionates, 2 atoms, of sulphur are mixed with the metallic sulphide.

Detection of Sulphur in the dry way, and before the blowpipe.—Pure sulphur, when heated on platinum foil, melts and volatilises entirely, burning with a blue flame, and being converted into sulphurous anhydride, SO^2, which is easily recognised by its smell. All the foregoing sulphur compounds, without exception, when heated on charcoal in the inner blowpipe flame with carbonate of sodium, or a mixture of 1 part borax and 2 parts carbonate of sodium, form sulphide of sodium, which is easily recognised by dissolving the fused mass in water, and testing the solution with nitroprusside of sodium; by treating the fused mass with a strong acid, when hydrosulphuric acid is evolved; or by moistening the fused mass and placing it on a clean piece of metallic silver, when the surface of the silver is marked with a black stain of sulphide of silver. Any sulphur compound, when heated on a platinum-wire, in the inner or reducing flame, with a bead of carbonate of sodium saturated with silica, gives a yellowish or reddish-brown transparent bead, according to the amount of sulphur contained in the compound.

For the detection of sulphur in organic compounds, the substance under examination is fused with solid caustic potash on a silver plate, on which, after the fused mass is moistened with water, a black stain remains if sulphur be present. Or the compound is decomposed by nitric acid, hydrochloric acid and chlorate of potassium, or by fusion with a mixture of nitre with an alkaline carbonate or hydrate (which, of course, must be free from sulphuric acid); and the resulting acid solution tested for sulphuric acid with chloride of barium. Many organic compounds containing sulphur, are decomposed by merely boiling with a solution of caustic potash, sulphide of potassium being formed, which may be detected either by acetate of lead, or nitroprusside of sodium.

5. **Chlorine.** Cl. Atomic weight, 35·5.

Found principally in combination with sodium, as chloride of sodium, or common salt, both in solution in sea-water, and in the solid state as rock-salt. At the ordinary temperature chlorine is a heavy gas of a yellowish green colour, and a most irritating smell: in presence of water it bleaches litmus, indigo, and other vegetable colours. It is readily soluble in water, forming a solution possessing the characteristic colour and smell of the gas, which is commonly called *chlorine-water*. This solution gives with *hydrosulphuric acid* a precipitate of sulphur; with *nitrate of silver*, chloride and chlorate of silver; with *acetate of lead*, chloride and peroxide of lead. Chlorine-water always contains hydrochloric and hypochlorous acids, owing to spontaneous decomposition. $Cl^2 + OH^2 = ClH + ClOH$. Hence all the chlorine cannot be removed from chlorine-water by nitrate of silver; for, after the separation of chloride of silver, hypochlorous acid remains in solution, and may be detected by its bleaching action on vegetable colours.

Acids and Oxides of Chlorine. a. *Hydrochloric Acid*, ClH. *Metallic Chlorides.*—Hydrochloric acid is a colourless gas, that fumes in contact with the air: it possesses a strong acid reaction and a suffocating smell. It is very readily absorbed by water: a saturated solution of it in water constitutes concentrated hydrochloric acid. This is a colourless liquid, fuming strongly on contact with air. When the concentrated acid is heated, only a portion of the dissolved gas can be driven off, dilute acid remaining. With all basic metallic oxides, hydrochloric acid forms metallic chlorides and water: with peroxides (as well as with chromates, chlorates, and hypochlorites), it evolves chlorine, especially on heating ($Mn^2\,O^2 + 4ClH = 2MnCl + 2OH^2 + Cl^2$): with nitric acid it evolves chlorine (Aqua-regia, p. 8). Pure hydrochloric acid does not bleach vegetable colours.

Metallic chlorides differ considerably in their physical properties. Some are liquid, or of the consistency of butter, and volatile without decomposition (chlorides of antimony, arsenic, tin): others are solid, fusible, and non-volatile (chlorides of silver, lead, potassium, sodium, barium): others are decomposed by heat into chlorine and the metal (chlorides of gold and platinum), or if heated in contact with air, into chlorine and the metallic oxide (chloride of iron). Most chlorides are soluble in water: chloride of silver, $ClAg$, and subchloride of mercury, $ClHg^2$, are insoluble; subchloride of copper,

$ClCu^2$, protochlorides of gold and platinum, $ClAu$, $ClPt$, are almost insoluble; chloride of lead, $ClPb$, and many oxychlorides, are difficultly soluble. (c) Aqueous solutions of chlorides give with *nitrate of silver*, a white curdy precipitate of chloride of silver, which becomes violet by exposure to light: it is insoluble in dilute acids, readily soluble in ammonia, whence it is reprecipitated by nitric acid: even in the most dilute solutions nitrate of silver gives an opalescence. The solution of chloride should be acidulated with nitric acid. This reaction distinguishes chlorides from all salts, except bromides, iodides, and cyanides. *Subnitrate of mercury* gives a white precipitate of subchloride of mercury, insoluble in water and dilute acids, readily soluble in chlorine-water and aqua-regia, blackened by ammonia. *Acetate of lead* gives, with a not too dilute solution of a chloride, a white crystalline precipitate of chloride of lead, soluble on boiling with excess of water, from which solution it crystallises on cooling. When heated with sulphuric acid, chlorides give off hydrochloric acid gas ($2ClNa + SO^4H^2 = SO^4Na^2 + 2ClH$): only the chlorides of mercury, silver, lead, and tin are decomposed with difficulty or not at all by sulphuric acid. With binoxide of manganese and sulphuric acid, chlorides evolve chlorine, easily recognised by its colour and smell. (c) When heated in the dry way with bichromate of potassium and sulphuric acid, chlorides evolve red fumes of *chlorochromic acid*, $Cr^2O^2Cl^2$, which give a yellow solution when passed into water or aqueous ammonia. Bromides when similarly treated also evolve red fumes; but these form a colourless solution in aqueous ammonia, and their solution in water is decolorised by heat.

Blowpipe reactions.—Chlorides give a blue colour to the outer flame, when heated with a bead of microcosmic salt (phosphate of sodium, ammonium, and hydrogen) saturated with oxide of copper.

b. *Perchloric Acid*, ClO^4H.—Formed by the primary decomposition of chlorate of potassium by heat or by sulphuric acid. ($2ClO^3K = ClK + O^2 + ClO^4K$.)

Aqueous solutions of perchloric acid or perchlorates do not bleach vegetable colours. All perchlorates are soluble in water; perchlorate of potassium is the least soluble, hence a strong solution of a perchlorate gives a crystalline precipitate with a potassium-salt. This precipitate is quite insoluble in alcohol. The alkaline and alkaline-earthy perchlorates, are decomposed by heat into chlorides and oxygen; they explode feebly when heated with charcoal. They are not decomposed by sulphuric acid in the cold, or by heating with hydrochloric acid, or any dilute acid; when heated with strong sulphuric acid, they are decomposed with difficulty, without the formation of any bleaching liquid. These reactions distinguish perchloric from other chlorine acids.

c. *Chloric Acid*, ClO^3H.—Formed by the action of chlorine on an aqueous solution of potash or soda ($3K^2O + Cl^6 = ClO^3K + 5ClK$). The aqueous solution of chloric acid is a colourless liquid, which first reddens and then bleaches litmus; it is decomposed by heat into perchloric acid, oxygen, and chlorine; it is readily deoxidised by hydrosulphuric, sulphurous, phosphorous, and hydrochloric acids, and by many organic compounds.

All chlorates are soluble in water; they cannot, therefore, be precipitated by any reagent, not even by nitrate of silver. Their aqueous solution does not bleach litmus. They are decomposed by heat, fusing and evolving oxygen, or a mixture of oxygen and chlorine, while in some cases a chloride, in others an oxide or a basic chloride, remains behind. When mixed with combustible bodies (as sulphur, phosphorus, carbon, or organic bodies generally), they explode violently on heating, rubbing strongly, or moistening with fuming sulphuric acid. If a fragment of a chlorate be brought into contact under water with phosphorus and strong sulphuric acid, the phosphorus takes fire. (c) When treated with strong sulphuric acid, even in the cold, chlorates give a brown or yellow colour, while a greenish-yellow gas, ClO^2, is evolved, which explodes if the mixture be heated ($3ClO^3K + 2SO^4H^2 = 2SO^4KH + ClO^4K + 2ClO^2 + H^2O$.) When chlorate of potassium is heated with hydrochloric acid, a yellow solution is formed, and a yellow gas evolved, which is a mixture of chlorine with some lower oxide of chlorine; this gas, which is commonly called euchlorine, explodes violently when heated. The solution is a powerful oxidising and dissolving medium.

The reducing action exercised by sulphurous acid on chloric acid, furnishes a test for the distinction of chloric from perchloric acid.

If a solution of a chlorate be heated with excess of sulphurous acid, the addition of nitrate of silver gives a white precipitate, composed of a mixture of sulphite and chloride of silver, which is not entirely dissolved on the addition of nitric acid. Perchlorates are not reduced by sulphurous acid ; hence, if their solutions be similarly treated, the precipitate caused by nitrate of silver, consisting entirely of sulphite of silver, is readily soluble in nitric acid.

d. *Peroxide of Chlorine* (hypochloric acid), ClO^2. — A greenish-yellow explosive gas, possessing a smell somewhat resembling that of burnt sugar. Its aqueous solution is decomposed at once into chloric and chlorous acids ($2\,ClO^2 + OH^2 = ClO^3H + ClO^2H$).

e. *Chlorous Anhydride*, Cl^2O^3.—Formed by the action of nitrous acid, or of nitric acid in presence of arsenious or tartaric acids, on chlorate of potassium. It is a yellowish-green gas that bleaches vegetable colours, and is readily decomposed by heat. It decolorises permanganate of potassium. It is readily soluble in water, forming

f. *Chlorous Acid*, ClO^2H.—Chlorites are very easily decomposed into chlorides and chlorates. Their solution gives a whitish yellow precipitate with *nitrate of silver* or *lead.* The former is soluble in excess of water.

g. *Hypochlorous Anhydride*, Cl^2O.—A dark yellow gas resembling chlorine in its smell and bleaching powers : it is decomposed by heat, with explosion, into chlorine and oxygen. It is readily soluble in water, forming

h. *Hypochlorous Acid*, $ClOH$.—When dilute, a colourless liquid; when concentrated, it has a yellow tinge. It is a most powerful bleaching agent. Hypochlorites generally occur as bleaching salts ; they are prepared by the slow action of chlorine at a low temperature upon the alkaline or alkaline-earthy hydrates (solutions of potash, soda, &c.). Thus obtained, they are always mixed with metallic chlorides ($Cl^2 + K^2O = ClOK + ClK$). The most familiar example of a hypochlorite is bleaching powder, commonly called *chloride of lime* ; it is a mixture of hypochlorite, chloride, and hydrate of calcium. Hypochlorites are very unstable, being decomposed even by carbonic acid, with liberation of hypochlorous acid. This property renders chloride of lime valuable as a disinfectant.

All hypochlorites are soluble in water; their solution has a caustic taste and a peculiar smell, somewhat resembling that of chlorine, which is owing to free hypochlorous acid. Their solution bleaches litmus, especially if the hypochlorous acid be set free by the addition of a mineral acid: it is also a powerful oxidising agent. Hypochlorites are decomposed by heat into chlorides and chlorates. (c) When treated even with very dilute acids, they evolve, if quite pure, hypochlorous anhydride; if mixed with chlorides (as in bleaching powder), chlorine ($ClCa + ClOCa + SO^4H^2 = SO^4Ca^2 + OH^2 + Cl^2$). Alkaline hypochlorites give with *proto-salts of manganese*, a gradual brown precipitate of peroxide of manganese; with salts of *lead*, first a precipitate of white chloride, then of brown peroxide, of lead; with *silver-salts*, chloride of silver; with *subsalts of mercury*, subchloride of mercury. If a solution of arsenious anhydride in hydrochloric acid is coloured by a few drops of an indigo solution, and a solution of a bleaching salt gradually added, the indigo is not decolorised by the chlorine evolved until the whole of the arsenious anhydride has been converted into arsenic anhydride. On this reaction is founded a method for the valuation of bleaching powder, by means of standard solutions of arsenious anhydride and of chloride of lime. (*See* p. 246.)

A striking analogy will be perceived between the above series of oxygen compounds of chlorine, and the corresponding series of oxides of nitrogen. Nor is the analogy confined to the existence of the same terms in each series; but the corresponding terms in each series are singularly analogous in many of their properties. Thus we find that *chlorates* and *nitrates* are alike soluble in water; that they are very readily deoxidised, and so are powerful oxidising agents, &c. It is not difficult, however, to distinguish between these two salts. Chlorates do not exhibit the reactions with protosulphate of iron, and sulphuric acid and copper filings, which are characteristic of nitrates: and alkaline and alkaline-earthy chlorates yield on ignition a residue whose solution is neutral to test-paper, and exhibits the reactions of a chloride, while the nitrates of the same metals leave an alkaline residue after ignition.

Hypochlorites are distinguished from the higher chlorine acids by the bleaching action of their aqueous solutions, either alone or on addition of the weakest acid.

Chlorides are distinguished from all other chlorine salts by their evolving hydrochloric acid gas, when heated with sulphuric acid, which reddens litmus strongly, but does not bleach it at all.

Detection of Chlorine in organic compounds. The most speedy method for ascertaining the presence of chlorine in organic compounds consists in introducing the compound under examination into the flame of a lamp, when, if chlorine be present, a green tinge will be given to the flame. There are but few organic compounds in which chlorine can be detected by means of nitrate of silver. In the great majority of cases the compound must be decomposed before chlorine can be detected in it by this reagent. This decomposition is best effected by heating the compound to redness with quick-lime, which must be freed from chloride of calcium by washing, and subsequently ignited, when, if chlorine be present in the compound, chloride of calcium is formed. The cooled mass is dissolved in dilute nitric acid, and the solution tested with nitrate of silver. By employing a known weight of the organic compound, and determining the weight of the chloride of silver obtained, the chlorine present may be accurately estimated by this method.

6. **Bromine.** Br. Atomic weight, 80.

Bromine is a dark-red heavy liquid: it boils at 47°, but at the ordinary temperature gives off red fumes which have a most offensive smell, and a peculiarly irritating action both on the lungs and eyes. It is somewhat soluble in water, giving a red or yellow solution, according to the degree of concentration; this solution decolorises litmus and indigo, gives with hydrosulphuric acid a precipitate of sulphur, with starch an orange-red colour, and generally resembles chlorine water in its behaviour to other reagents. It combines readily with most metals, forming metallic bromides.

ACIDS OF BROMINE. a. *Hydrobromic Acid*, BrH. *Metallic Bromides.*—Hydrobromic acid is a colourless gas, which, like hydrochloric acid, is very soluble in water, the behaviour of the colourless solution when heated exactly resembles that of the aqueous solution of hydrochloric acid.

Bromides generally very closely resemble chlorides in their reactions. With *nitrate of silver*, their solution gives a yellowish white curdy precipitate of bromide of silver, BrAg, which is insoluble in dilute nitric acid, soluble in ammonia, but less easily than the chloride; easily soluble in cyanide of potassium, or hyposulphite of sodium. If the precipitate of BrAg, after pouring off the supernatant liquid, be treated with strong hydrochloric acid, the mixture becomes red, and when heated evolves vapours of bromine. *Subnitrate of mercury* gives a yellowish white precipitate of sub-bromide of mercury, $BrHg^2$, insoluble in dilute nitric acid, readily soluble in chlorine-water, giving a deep yellow solution. *Acetate of lead* gives a white precipitate of bromide of lead, BrPb, less soluble than the chloride in excess of water, readily soluble in nitric acid. When heated with concentrated nitric acid, bromides evolve dark-red bromine vapours; with sulphuric acid, hydrobromic acid, together with bromine and sulphurous anhydride; with sulphuric acid and binoxide of manganese, nothing but bromine, which may be detected, if present in too small a quantity to be visible to the eye, by the orange-red colour which it gives to a piece of paper moistened with starch-paste, and held to the mouth of the tube.

Sulphuric acid containing peroxide of nitrogen, or a mixture of nitrite of potassium and hydrochloric acid, separates no bromine from metallic bromides. All bromides are decomposed by free chlorine, or by hydrochloric acid, a chloride being formed and bromine set free. (c) If chlorine-water be added to a solution of a bromide, or to a solid bromide (as BrAg), the solution is coloured yellow by the bromine set free; and if it be now agitated with a little ether, the ether will dissolve all the bromine, forming a yellow or red layer at the top of the liquid. By comparing the colour of this layer with that of a standard ethereal solution of bromine, the quantity of bromine present may be approximately estimated. The ethereal solution of bromine is decolorised by solution of potash, with formation of bromide and bromate of potassium; and the alkaline solution, when distilled with sulphuric acid, gives off vapours of bromine. If very little bromine be present, it is advisable to evaporate the solution under examination to dryness, to treat the residue with alcohol, filter, evaporate the alcoholic solution to dryness, dissolve the residue in as little water as possible, and treat this solution with chlorine-water and ether. When the quantity of bromine is very small, only a drop of chlorine-water should be added. This is the method usually employed for the detection of bromine in mineral waters. This reaction does not distinguish bromine from iodine.

Blowpipe reactions.—With a bead of microcosmic salt and oxide of copper, bromides give a blue colour to the outer flame, which has a somewhat greener tinge than the colour similarly produced by chlorides.

Bromides are most readily distinguished from chlorides, by their reactions with sulphuric acid and chlorine. From a solution containing both salts, the whole of the bromide may be precipitated by careful addition of nitrate of silver, while some of the chloride still remains in solution.

b. *Bromic Acid*, BrO^3H.—This is the only oxygen acid of bromine known.

Bromates generally closely resemble chlorates in their reactions, especially in exploding when heated with charcoal, or other combustible substances. When heated alone, bromates evolve oxygen, (and sometimes bromine,) a metallic bromide being left. A solid bromate, heated with *sulphuric acid*, evolves bromine and oxygen; a solution of a bromate is coloured red, even by dilute sulphuric acid. With concentrated *hydrochloric acid*, bromates yield chloride of bromine, and form a yellow solution. A not too dilute solution of a bromate gives, with *lead-salts*, a white precipitate; with *subsalts of mercury*, a yellowish white precipitate, insoluble in nitric acid in the cold; with *silver-salts*, a white precipitate, almost insoluble in water, difficultly soluble in dilute nitric acid, easily soluble in ammonia. This precipitate is distinguished from chloride of silver by its evolving red vapours of bromine when heated with hydrochloric acid.

The reactions with silver-salts and with sulphuric acid, distinguish bromates from chlorates.

In organic compounds, bromine is detected by the methods already described in the case of chlorine (p. 30).

7. **Iodine.** I. Atomic weight, 127.

Iodine, at the ordinary temperature, is a greyish-black metallic-looking solid, which gives off deep violet fumes on a slight elevation of temperature. It has an unpleasant smell, somewhat resembling that of chlorine. It stains the skin a deep yellow or brown. It is very slightly soluble in water, very readily in alcohol, ether, iodide of potassium, and hydriodic acid, forming brown solutions; and in bisulphide of carbon, CS^2, with a magnificent violet colour, which is so intense as to afford one of the most delicate reactions for the detection of free iodine. It is also soluble, with a red colour, in chloroform, benzol, and petroleum. It is soluble in hyposulphite of sodium, with formation of tetrathionate of sodium ($2S^2O^3Na^2 + I^2 = S^4O^6Na^2 + 2INa$); with very dilute sulphurous acid it forms sulphuric and hydriodic acids; with hydrosulphuric acid it forms hydriodic acid, and separates sulphur. Iodine has a slight bleaching action on vegetable colours, but in a degree very inferior to either chlorine or bromine. Free iodine in solution forms a deep blue compound with starch solution, the colour of which is destroyed by heat; the smallest traces of free iodine may be thus detected. It combines with most metals, forming metallic iodides.

ACIDS OF IODINE. a. *Hydriodic Acid*, HI. *Metallic Iodides.*—Hydriodic acid is a colourless gas, readily soluble in water, forming a colourless solution, which, when heated, behaves like the solutions of hydrochloric and hydrobromic acids. Its aqueous solution absorbs oxygen from the air, water being formed and iodine set free, which dissolves in the undecomposed acid, and colours the solution brown.

Alkaline, and alkaline-earthy iodides, are soluble in water: most other metallic iodides are insoluble. The alkaline iodides are not decomposed when heated in the air: other iodides are partially decomposed by heat, iodine-vapours being given off, and a metallic oxide left. When heated with sulphuric acid, iodides give off iodine-vapours and sulphurous anhydride: by the addition of binoxide of manganese, the evolution of sulphurous anhydride is prevented. (c) *Nitrate of silver* gives with solutions of iodides a yellowish-white precipitate of iodide of silver, IAg, insoluble in common nitric acid, almost entirely insoluble in ammonia, which destroys its yellow tinge; soluble in cyanide of potassium, soluble also when boiled with *strong* fuming nitric acid, iodine being set free. *Subnitrate of mercury* gives a yellowish-green precipitate of subiodide of mercury, IHg^2, insoluble in dilute nitric acid, soluble in iodide of potassium. *Protosalts of mercury* give a vermilion-red precipitate of iodide of mercury, IHg, soluble in excess either of the mercury salt or of the iodide: this precipitate, when dried and heated, becomes yellow. (c) *Lead-salts* give a bright yellow precipitate of iodide of lead, IPb, soluble on boiling with excess of water, from which solution it crystallises on cooling in beautiful shining yellow scales: soluble in dilute nitric acid. (c) *Nitrate of palladium* gives a black precipitate of iodide of palladium, IPd, insoluble in cold hydrochloric or nitric acid, soluble in ammonia: this reagent serves to separate iodine from chlorine and bromine, and to estimate iodine. Iodine is also completely precipitated from solutions of iodides by a mixture of 1 part *sulphate of copper*, and 2½ parts *protosulphate of iron*, or by a mixture of sulphate of copper with sulphurous acid, as dirty-white subiodide of copper, ICu^2. Neither chlorides nor bromides are precipitated by this reagent.

Iodides, whether solid or in solution, are easily decomposed by chlorine, bromine, strong nitric acid, nitrous acid, peroxide of nitrogen, peroxide of barium and hydrochloric acid, strong sulphuric acid, or sulphuric acid and binoxide of manganese: in all these cases iodine is separated, and, according to the quantity and form of the iodide employed, is either precipitated as a black powder, dissolved, forming a brown solution, or given off in characteristic violet fumes. (c) When this iodine, however set free, comes into contact with solution of starch, a blue compound is formed (if very little iodine be present, the colour is violet or rose-red; if excess of iodine, green), which affords the most delicate test for the detection of iodine. The best way to apply this test for the detection of very small traces of iodine, is to add to the liquid under examination (which must be neutral or slightly acid) a drop of solution of starch, and to pass into it the nitrous fumes evolved by the action of nitric acid on metallic copper: if the slightest trace of an iodide be present, a violet or reddish tinge will at once be produced. Instead of starch, bisulphide of carbon may be added to the iodide-solution that has been decomposed by any of the above reagents, which, on agitation, will dissolve the free iodine, giving a violet colour. The free iodine may also be dissolved by ether: but the colour of the solution so closely resembles that of bromine, that iodine cannot be detected by this method in presence of bromine. Solutions containing very little iodide should be evaporated and treated with alcohol, as described in the case of bromides (p. 32). Chlorine-water, which is often used instead of nitrous fumes to decompose the iodide, has this disadvantage, that excess of it forms chloride of iodine, and destroys the blue colour of iodide of starch, and the violet colour of the bisulphide of carbon solution: when it is employed for the detection of traces of iodine, it should be in a very dilute solution, or, better still, a little of the gas from an open bottle of chlorine-water should be allowed to come in contact with the surface of the iodide solution. Insoluble compounds are examined for iodine by moistening them in a stoppered bottle with strong sulphuric acid, introducing a slip of paper moistened with starch-paste between the neck and stopper of the bottle, and allowing it to remain for some hours, when it will be coloured violet if the smallest trace of iodine be present. The blue colour of iodide of starch is destroyed by alkalis, by hydrosulphuric, sulphurous, or arsenious acids, by chloride of tin or chloride of mercury, or by any reducing organic body. The blue colour, when destroyed by alkalis, may be restored by any dilute acid (even acetic), but not by chlorine-water. Heat also destroys the blue colour, which, however, reappears on cooling.

Blowpipe reactions.—With a bead of microcosmic salt and oxide of copper, iodides colour the outer flame emerald-green.

b. Periodic Acid, IO^4H.—Formed by the action of chlorine on an alkaline solution of iodate of sodium ($IO^3Na+2Cl+NaHO=IO^4Na+ClNa+ClH$). It is a crystalline body: it is decomposed by heat into oxygen and iodine-vapours. It forms basic as well as normal salts.

Periodates are very stable salts. Their solution gives with *barium-* and *lead-*salts white precipitates soluble in dilute nitric acid; with *silver-salts* a brown precipitate soluble in dilute nitric acid and ammonia. Periodates when heated generally behave like iodates.

c. *Iodic Acid*, IO^3H. — Formed by dissolving iodine in solutions of potash or soda ($3K^2O+I^6=IO^3K+5IK$): by the action of concentrated nitric acid on iodine, or of carbonate of sodium on chloride of iodine. It is a crystalline body, decomposed by heat into oxygen and iodine-vapours: readily soluble in water. It is instantaneously reduced by hydrosulphuric, sulphurous, and hydriodic acids, and nitric oxide, iodine being set free, which may be detected by means of starch.

Only the alkaline iodates are soluble in water. They are decomposed by heat, giving off oxygen (and in some cases iodine-vapours) and leaving a residue of iodide. Their solutions give white precipitates with salts of *barium*, *lead*, and *silver*, and *subsalts of mercury:* iodate of silver is insoluble in dilute nitric acid, soluble in ammonia, whence sulphurous acid throws down iodide of silver. Soluble iodates are decomposed by *hydrosulphuric acid*, an iodide and sulphuric acid being formed, and sulphur deposited: *sulphurous acid* separates iodine, soluble in excess of the reagent: *hydrochloric acid* forms chloride of iodine: solution of *indigo* is decolorised on addition of sulphuric acid. A solution of an iodate containing iodide of potassium is decomposed by the weakest acids (even acetic), iodine being set free, which may be detected by starch paste. This reaction serves to detect iodic acid in iodide of potassium. Iodates are not decomposed when heated with strong sulphuric acid, unless some reducing agent (as protosulphate of iron) be present: in which case iodine-vapours are given off. Iodates explode when heated with charcoal, but more feebly than chlorates or bromates.

Iodates are distinguished from all other salts, except periodates, by their liberating iodine when treated with reducing agents. Periodates are so much more stable than iodates, that hydrosulphuric acid is the only agent by which they can be reduced, with liberation of iodine. Periodates can always be distinguished from iodates by means of nitrate of silver.

The mode of detecting iodine in organic compounds is the same as that adopted for chlorine and bromine (p. 30).

Separation and estimation of Chlorine, Bromine, and Iodine.— For the detection of a bromide in presence of an iodide, the iodine is first removed by decomposing the iodide by a mixture of fuming nitric acid with sulphuric acid, and dissolving out the iodine by repeated agitation with ether. The ethereal solution of iodine is then removed, and chlorine-water carefully added to the remaining liquid, which is again agitated with ether, which dissolves out the bromine. Small quantities of a chloride in presence of excess of bromide, are best detected by distilling the dry salts with bichromate of potassium and fuming sulphuric acid, and leading the vapours evolved into aqueous ammonia, which, if a chloride be present, is coloured yellow, owing to the formation of chromate of ammonium, while, if only a bromide be present, it remains colourless. Small traces of a chloride in presence of an iodide cannot be detected in this manner. The best method in this case is to precipitate the chlorine and iodine together by nitrate of silver, digest the precipitate with ammonia, filter, and add nitric acid to the filtrate, when an opalescence will be produced, if the smallest trace of a chloride be present. A solution of chloride of silver in ammonia gives no precipitate with a metallic chloride, but with an iodide it gives a precipitate of iodide of silver.

For the quantitative separation of chlorine, bromine, and iodine in solutions containing chlorides, bromides, and iodides, the iodine is first removed by nitrate of palladium, and the black precipitate of IPd collected after 12 hours on a weighed filter, dried, and weighed. (The iodine may be removed, though with somewhat less accuracy by the mixture of sulphate of copper and protosulphate of iron (p. 34); the subiodide of copper is dried at 120° and weighed.) The excess of palladium is then removed from the solution by hydrosulphuric acid, and the excess of hydrosulphuric acid by sesquisulphate of iron which is perfectly free from chloride, and the bromine together with a portion of the chlorine removed by fractional precipitation by nitrate of silver. The precipitate is dried and weighed, fused in a stream of chlorine, and the bromine determined by its loss in weight. Or the weighed mixture of chloride and bromide is reduced by clean metallic zinc, with addition of a few drops of hydrochloric acid, and when the reduction is complete the resulting metallic silver is weighed. If a standard solution of nitrate of silver (*i. e.* a known quantity of silver) be employed for the precipitation, the bromine may be calculated at once from the weight of the precipitate. The rest of the chlorine is then completely precipitated by nitrate of silver, and the resulting ClAg dried, ignited, and weighed.

Iodine and its lower chlorine-compounds impart an intense violet colour to bisulphide of carbon; pentachloride of iodine, ICl^5, does not. Hence, the colour disappears as soon as the pentachloride is formed. On this reaction is founded a volumetric method for estimating iodine in presence of chlorine and bromine (p. 254).

8. **Cyanogen.** CN. Cy. Atomic weight, 26.

This substance, though not an elementary body, exhibits such striking analogies with chlorine, bromine, and iodine, that it may be most fitly treated of in connection with them. It is a colourless condensible gas, with a peculiar smell resembling that of peach-kernels, and irritating the eyes as well as the nose. It is combustible, burning with a violet-blue flame. It is moderately soluble in water, much more so in alcohol: these solutions undergo decomposition, even in stoppered bottles, especially if exposed to the light; they assume a brown colour, and are found to contain carbonic, oxalic, and hydrocyanic acids, ammonia, urea, and paracyanogen (a brown substance which is isomeric with cyanogen). Cyanogen is completely absorbed by solution of potash, and (more slowly) by moist oxide of mercury.

ACIDS OF CYANOGEN. *Hydrocyanic or Prussic Acid,* CyH. *Metallic Cyanides.*—Hydrocyanic acid is a transparent, combustible, very volatile liquid (boiling at 26°), with a peculiar smell, resembling that of bitter almonds. It is the most deadly poison known. In the pure state it is decomposed even in closed vessels, depositing paracyanogen. It is a very weak acid, reddening litmus feebly, and not decomposing carbonates. By alkalis or strong acids, it is decomposed into formic acid and ammonia, which latter remains combined with the acid employed ($CNH + 2OH^2 = CHO^2H + NH^3$). It is soluble in all proportions in water, alcohol, and ether; its solution is gradually decomposed by light, even in closed vessels, though less rapidly than the pure acid.

The alkaline and alkaline-earthy cyanides are readily soluble in water; in the solid state they absorb moisture from the air, and deliquesce; their solution has an alkaline reaction, and smells of hydrocyanic acid, and is decomposed even by the weakest acids hydrocyanic acid being set free. The cyanides of the heavy metals are mostly insoluble in water (cyanide of mercury is soluble), and are not decomposed by oxygen acids; hydrochloric or hydrosulphuric acid decomposes them, liberating hydrocyanic acid. The cyanides of potassium and sodium are not decomposed by ignition in closed vessels; but when heated in contact with oxygen, they take it up, and are converted into cyanates. This property renders them valuable agents for reducing metallic oxides and sulphides to the metallic state. The behaviour of the cyanides of the heavy metals on ignition, is very various. Cyanide of mercury yields cyanogen, paracyanogen, and mercury; others yield nitrogen, and a metallic carbide, or cyanogen and a metallic subcyanide (or paracyanide). The alkaline cyanides form soluble double cyanides, with those of many heavy metals. Thus the cyanides of *gold*, *palladium*, *silver*, *copper*, *cadmium*, *nickel*, *iron*, *chromium*, *manganese*, *cobalt*, *zinc*, &c., are readily soluble in cyanide of potassium. The solution, which contains a double cyanide of potassium and the heavy metal, is not precipitated by an alkaline hydrate or carbonate; in some cases (the double cyanides of *silver*, *mercury*, and *cadmium*) the heavy metal is readily precipitated as sulphide by hydrosulphuric acid; in others (those of *manganese*, *nickel*, *zinc*, and *copper*) the sulphide is only partially precipitated; in others (those of *iron* and *cobalt*), it is not precipitated at all.

Nitrate of silver gives with a solution of a cyanide a white, curdy precipitate of cyanide of silver, $CyAg$, insoluble in dilute nitric acid, soluble in ammonia, hyposulphite of sodium, cyanide of potassium, and concentrated nitric acid. This precipitate is distinguished from chloride, bromide, and iodide of silver, which it closely resembles, by its giving off the smell of hydrocyanic acid when treated with concentrated hydrochloric acid; and by its decomposition by heat into cyanogen, and a mixture of paracyanogen and metallic silver, while the other salts fuse without decomposition. The superior volatility of hydrocyanic acid also enables us to detect it in presence of the other three acids. If a solution containing free hydrocyanic acid be placed in a watch-glass, and another watch-glass moistened with nitrate of silver be inverted over it, a deposit of cyanide of silver will speedily be formed in the upper glass, even at the ordinary temperature; while no precipitate is formed in similar circumstances by the other three acids. To obtain this reaction, the acid must be free; therefore, if a solution of a cyanide be employed, it must be first decomposed by a stronger acid. *Subsalts of mercury* give a grey precipitate of metallic mercury, while cyanide of mercury remains in solution ($2CyH + OHg^4 = 2CyHg + Hg^2 + OH^2$). (c) *Proto-salts of mercury* give no precipitate, cyanide of mercury being soluble; if the solution be boiled with oxide of mercury, a basic cyanide is formed, which is alkaline to test-paper. No other acid exhibits this reaction. *Sulphate of copper*, containing sulphurous acid, gives a white precipitate of subcyanide of copper, $CyCu^2$, soluble in cyanide of potassium. *Iron-salts* give no precipitate with free hydrocyanic acid. With cyanide of potassium *sesquichloride of iron* precipitates sesquihydrate of iron, hydrocyanic acid being set free. *Protosalts of iron*, if quite free from sesquisalt, give a yellowish-red precipitate ($CyFe$?), soluble in excess of cyanide of potassium, especially on addition of potash: the solution contains *ferrocyanide of potassium.* Hereon is founded one of the best methods for detecting hydrocyanic acid. (c) Potash is first added to the liquid under examination, and then a mixture of proto- and sesquisalt of iron (protosulphate of iron that has been exposed some time to the air, answers the purpose), and finally excess of hydrochloric acid, which dissolves the oxides of iron which have been precipitated by the potash, and leaves behind a dark blue precipitate of Prussian blue. If mere traces of cyanide be present, there is no immediate precipitate, but the solution has a green colour, and deposits Prussian blue after long standing. (c) The following reaction is even more delicate, if possible. Add to the solution under examination (in a small porcelain basin) a drop or two of yellow sulphide of ammonium, and evaporate to dryness on a water-bath ; if even a trace of a cyanide be present, sulphocyanate of ammonium will be formed, which, when the dry residue is dissolved in alcohol and a drop of sesquichloride of iron added, gives a deep red colour. A solution containing free hydrocyanic acid dissolves *oxide of mercury*, forming cyanide of mercury, and the solution is not precipitated by alkalis, but hydrosulphuric acid precipitates black sulphide of mercury ; very small quantities of hydrocyanic acid may be detected in this manner. If the solution contains any free hydrochloric acid, the addition of ammonia gives a precipitate of subchloride of mercury. If a solution containing free hydrochloric and hydrocyanic acids be evaporated to dryness with borax, the hydrocyanic acid alone volatilises, and hydrochloric acid may be detected in the residue by means of nitrate of silver.

When heated with concentrated sulphuric acid, cyanides are decomposed into a metallic sulphate, sulphate of ammonium, and carbonic oxide ($2CNM + 2SO^4H^2 + 2H^2O = SO^4M^2 + SO^4(NH^4)^2 + 2CO$). All cyanogen compounds are decomposed when heated to redness with oxide of copper, yielding 2 vols. carbonic anhydride and 1 vol. nitrogen. Many double cyanides, whether soluble or insoluble, which cannot be otherwise decomposed, may be decomposed by prolonged heating with aqua-regia, or fuming nitric acid ; or by fusion with three or four times their weight of a mixture of 3 parts sulphate and 1 part nitrate of ammonium ; the heavy metal may then be detected in the residue by the usual reagents.

Estimation of Hydrocyanic Acid (see p. 257).

b. *Cyanic Acid*, CyOH.—(c) Cyanates are easily recognised by their decomposition when treated with strong acids, carbonic anhydride being evolved with effervescence, accompanied by the penetrating smell of undecomposed cyanic acid, while the ammonium-salt of the acid employed remains in solution ($CNOH + ClH + OH^2 = CO^2 + ClNH^4$). Alkaline cyanates are not decomposed by heat in the dry way; their aqueous solution is readily decomposed, especially when heated, into an acid carbonate and ammonia ($CNOK + 2OH^2 = CO^3KH + NH^3$). *Nitrates of lead* and *silver* and *subnitrate of mercury* give a white precipitate with cyanates; *nitrate of copper*, a greenish-brown precipitate; *terchloride of gold*, a brown precipitate. When evaporated to dryness with sulphate of ammonium, cyanates yield urea, CH^4N^2O ($2CNOK + SO^4(NH^4)^2 = 2CH^4N^2O + SO^4K^2$).

c. There are two other oxygen acids of cyanogen, both isomeric with cyanic acid,—*Fulminic Acid*, $Cy^2O^2H^2$; and *Cyanuric Acid*, $Cy^3O^3H^3$. Fulminic acid is only known in its silver and mercury salts. They are very dangerous compounds, exploding most violently by heat, percussion, or contact with strong sulphuric acid. Cyanuric acid is a very stable acid. Its salts are decomposed when heated with an alkali, forming aqueous cyanic acid, cyanate of ammonium, carbonic anhydride, nitrogen, and leaving a residue of alkaline cyanate.

d. *Sulphocyanic Acid*, CySH.—This acid is found in the saliva. Most sulphocyanates are soluble in water and alcohol. They give white precipitates, with a mixture of *sulphate of copper* and *sulphurous acid*, with salts of *silver* and *gold*, and *subsalts of mercury*. Sulphocyanate of silver, CySAg, is insoluble in dilute nitric acid, and may be employed for the estimation of sulphocyanic acid in soluble compounds. (c) With *sesquichloride of iron*, sulphocyanates give an intense blood-red colour, visible even in the most dilute solutions. This coloration is not destroyed by excess of hydrochloric acid, but disappears on addition of chloride of mercury: if metallic zinc be immersed in the red solution, hydrosulphuric acid is evolved. These reactions distinguish sulphocyanic acid from meconic, and some other organic acids, which give a similar red colour with persalts of iron. Most sulphocyanates are decomposed by heat into nitrogen, cyanogen, bisulphide of car bon, and a metallic sulphide. ($4CNSM = N + 3CN + CS^2 + 2M^2S$.)

Double Cyanides.—We have already observed (p. 39) that the cyanides of many of the heavy metals are soluble in cyanide of potassium, forming double cyanides of the heavy metal and potassium, in which the heavy metal cannot be detected by any of the ordinary reagents. This peculiarity of behaviour on the part of the heavy metal in these salts has led to the adoption of the theory, that it is combined with the cyanogen so as to form a distinct compound radical. Thus, the cyanide of iron and potassium, Cy^3FeK^2, has been regarded as the salt of a distinct radical—ferrocyanogen, Cy^3Fe—which, like cyanogen itself, combines with hydrogen to form an acid, and with other metals to form a series of salts. Hence the names ferrocyanide of potassium, &c., generally applied to this class of salts. We, however, shall regard these bodies merely as double cyanides, which they undoubtedly are. Some of them exhibit so remarkable a behaviour with several metals, that it is necessary to enumerate their most important reactions.

Protocyanide of Iron and Potassium (ferrocyanide of potassium, yellow prussiate of potassium), $Cy^3FeK^2 = (CyFe + 2CyK)$.—The double cyanides of iron and the alkaline metals are soluble in water. When anhydrous, they are colourless; but are yellow when they contain water of crystallisation. The double cyanides of iron, and most other metals, are insoluble in water, many of them in acids also. Some of them are white (as those of the earthy metals, zinc, lead, silver, mercury); others are distinguished by peculiar colours, whence the cyanide of iron and potassium is much used as a reagent for the detection of several metals, especially of iron and copper. With *sesquisalts of iron* it gives a blue precipitate, Cy^9Fe^7; with *protosalts of iron*, a white or bluish-white precipitate, Cy^6Fe^5K; with *protosalts of copper*, a brownish-red precipitate, Cy^3FeCu^2.

Sesquicyanide of Iron and Potassium (ferricyanide of potassium, red prussiate of potassium), $Cy^6Fe^2K^3 = (Cy^3Fe^2 + 3CyK)$.—The double sesquicyanides of iron and the alkaline metals are soluble in water, and have a yellowish-red colour. Their aqueous solution gives with *protosalts of iron* a dark-blue precipitate, Cy^6Fe^5; with *sesquisalts of iron*, no precipitate, or change of colour. If, however (as is always the case in practice), the least trace of a protosalt be present in either reagent, a dark-coloured solution is produced.

The soluble double cyanides of iron are decomposed by boiling with dilute sulphuric acid, a portion of their cyanogen being separated as hydrocyanic acid ($2Cy^3FeK^2 + 3SO^4H^2 = 3CyH + 2CyFe + CyK + 3SO^4KH$). With strong sulphuric acid, all double cyanides of iron evolve carbonic oxide. With caustic alkalis, all insoluble ferro- and ferricyanides are decomposed, with separation of the oxide of the basic metal, and formation of a double cyanide of iron and an alkaline metal. When fused with carbonate of potassium, cyanide and cyanate of potassium are formed, and the heavy metal reduced. When heated with sulphate of ammonium, they are all readily and completely decomposed (p. 41).

Nitroprusside of Sodium, $Cy^5NOFe^2Na^2$, which we have already mentioned (p. 17) as a reagent for the detection of soluble sulphides, is formed by the action of nitric acid on the double cyanide of iron and potassium.

Sesquicyanide of Cobalt and Potassium (cobalticyanide of potassium), $Cy^6Co^2K^3$.—An aqueous solution of sesquicyanide of cobalt and potassium is not decomposed by boiling with dilute sulphuric, nitric, or hydrochloric acid, by chlorine in presence of free alkali, or by oxide of mercury; while a solution of sesquicyanide of nickel and potassium is decomposed by these reagents. (Separation of Nickel from Cobalt, p. 148.) The soluble double cyanides of cobalt give, with *protosalts of copper*, a light blue precipitate; with *protosalts of nickel*, a greenish-blue precipitate; with *protosalts of cobalt*, a reddish precipitate; with *protosalts of iron* and *subsalts of mercury*, a white precipitate. These precipitates are mostly soluble in dilute acids, and easily decomposed by alkalis. By heating with concentrated sulphuric acid, or better, with sulphate and nitrate of ammonium, all the double cyanides of cobalt are completely decomposed.

9. **Fluorine.** F. Atomic weight, 19.

Fluorine has never been obtained in the free state. It occurs native chiefly as fluorspar, FCa, or as cryolite, $Al^2Na^3F^6$; it is also a constituent of several native phosphates and silicates (*e.g.* wavellite, topaz, mica, tourmaline, hornblende, &c.): it exists also as fluoride of calcium in bones and teeth, in mineral springs, and in the ashes of several plants.

ACIDS OF FLUORINE. *Hydrofluoric Acid,* FH. *Metallic Fluorides.*—Hydrofluoric acid is a colourless liquid, extremely volatile (boiling at 15° C): on contact with air it gives off abundant fumes, of a very suffocating smell : it is miscible with water in all proportions. Its most characteristic property is that of readily dissolving silica and silicates, and consequently of corroding glass and rendering it opaque: hence it is employed for the decomposition of silicates, and hereon is founded the only certain method for the detection of fluorine. Hence too glass vessels cannot be employed in its preparation. By its action on silica, fluoride of silicon, SiF^4, is formed, which combines with 2 additional atoms of hydrofluoric acid, forming fluosilicic acid, SiF^6H^2 ; by its action on a silicate, a metallic fluosilicate is formed, and (according to the proportions of silica and metal contained in the silicate) either a metallic fluoride or fluoride of silicon. Boric, tantalic, titanic, molybdic, and tungstic acids are similarly decomposed and dissolved by hydrofluoric acid, with formation of compounds analogous to fluosilicic acid. It does not act upon gold or platinum, and very slightly upon lead.

Metallic fluorides possess very various physical properties. Some are liquid and volatile, some solid and non-volatile: they are mostly insoluble, or very slightly soluble, in water. Soluble fluorides give with *chloride of calcium* a gelatinous precipitate of FCa, which becomes more distinctly visible on heating and on addition of ammonia: it is somewhat soluble in ammoniacal salts, and in dilute nitric or hydrochloric acids, less so in acetic acid, insoluble in free hydrofluoric acid. With *lead-salts* they give a white precipitate, of FPb, soluble in nitric acid ; with *silver-salts* they give no precipitate. All fluorides are decomposed by strong sulphuric (not by nitric) acid, hydrofluoric acid being evolved: fluorspar when thus treated is reduced to a pasty mass which does not moisten glass, and only evolves gaseous hydrofluoric acid on the application of heat. Many insoluble fluorides (*e. g.* FCa) are not completely decomposed by fusion with an alkaline carbonate, unless silica be also present.

For the qualitative detection of fluorine in bones, teeth, and minerals free from silica, the substance is finely powdered and mixed to a paste with strong sulphuric acid, in a good-sized platinum crucible. The crucible is then covered with a watch-glass, whose convex side has been coated with wax, and marked with lines drawn with the point of a knife, so as to leave the glass exposed in parts, and a gentle heat is applied. A little water should be placed in the hollow of the watch-glass, to prevent the wax from being melted by the heat. After some hours the wax is carefully removed from the watch-glass, when, if fluorine were present in the substance, the glass will be found corroded and made opaque in those portions which were not protected by the wax. If only very small traces of fluorine be present, the marks on the glass may not be at once perceptible; but they will be made visible at once by breathing on the convex side of the glass, which has previously been carefully dried. If the substance to be examined for fluorine contain silica, it is fused with carbonate of sodium, the fused mass dissolved in water, the silica precipitated from the solution by carbonate of ammonium and filtered off, the filtrate neutralised with acetic acid, and chloride of calcium added to it. The precipitate thus obtained, which will contain all the fluorine, is collected, and treated as above with sulphuric acid. Or the finely divided substance may be heated in a glass flask, with strong sulphuric acid and a fragment of marble; and the gases evolved, consisting of fluoride of silicon and carbonic anhydride, conducted into aqueous ammonia. The ammoniacal solution is then evaporated to dryness, the residue treated with water, and whatever remains undissolved removed by filtration; the filtrate again evaporated, and the residue examined for fluorine as above. This method is only applicable to silicates in which the proportion of fluorine is very small as compared with the silica; if the substance contains excess of fluorine, finely powdered silica must be added to it before this process can be employed.

Blowpipe reactions.—When a fluoride is heated before the blowpipe with microcosmic salt at one end of a glass tube, open at both ends, in such a manner that the flame is partially carried through the tube, vapour of water is given off, together with hydrofluoric acid, which may be detected by its action on the glass, and by its turning yellow a strip of fernambuc paper, held to the mouth of the tube. Many silicates containing fluorine, *e. g.* mica, tourmaline, give off fluoride of silicon when heated alone.

Estimation of Fluorine.—For the determination of fluorine in insoluble compounds containing phosphoric acid, the substance is fused with carbonate of sodium and silica, the fused mass treated with water, and the silica removed from the aqueous solution by carbonate of ammonium: the filtrate is then nearly neutralised by acetic acid, and the phosphoric acid and fluorine together precipitated by chloride of calcium. The precipitate, besides phosphate and fluoride, contains also some carbonate of calcium, to remove which it is ignited, saturated with acetic acid, dried in a water-bath, and thoroughly washed with water; and then ignited and weighed. The fluorine is then driven off by heating with concentrated sulphuric acid, alcohol is added to the residue in order to precipitate completely the sulphate of calcium formed, and the phosphoric acid determined in the filtrate as phosphate of magnesium and ammonium.

10. **Boron.** B. Atomic weight, 14·5.

Occurs in nature in the form of boric acid, either free (as sassolin), or combined with metals (tincal, boracite, datolite), and in smaller quantities in tourmalin, axinite, apyrite, rhodizite, &c. Boron is a dark powder, which burns when heated in the air, combining with oxygen, and forming boric anhydride.

OXIDES AND ACIDS OF BORON. a. *Boric Anhydride*, BO^2.—A colourless, transparent, glassy solid, that fuses when heated alone, but does not volatilise at all. It is soluble in water and alcohol, and its solution deposits crystals of

b. *Boric Acid*, BO^3H^2.—Scaly crystals, of a pearly lustre, greasy to the touch. It is less soluble in water than BO^2. The aqueous solution feebly reddens litmus: yellow turmeric paper moistened with it assumes a distinctly brown colour when dried. When its aqueous solution is evaporated, the boric acid partly volatilises with the vapour of water: this volatilisation is completely prevented by the addition of excess of carbonate of sodium, but not completely by ammonia, ammoniacal salts, or oxide of lead. When evaporated and ignited with chloride of ammonium, boric acid is partially converted into infusible nitride of boron, NB. The alcoholic solution of boric acid burns with a green flame, on which property is founded a method of detecting the acid.

The alkaline borates are readily soluble in water. The solution, whether of the normal or acid salt, has an alkaline reaction; it absorbs carbonic and sulphurous anhydrides, hydrosulphuric acid, and chlorine abundantly, and dissolves large quantities of sulphur, arsenious acid, and fatty organic acids. When an alkaline borate is evaporated to dryness with hydrochloric acid, the alkaline metal is entirely converted into chloride, and its amount may be determined as chloride of silver. Most other borates are difficultly soluble in water: none however are absolutely insoluble, so that boric acid cannot be entirely precipitated from a solution of a borate by any metallic salt. A not too dilute solution of a borate gives with salts of *calcium*, *barium*, *lead*, *silver*, *subsalts of mercury*, *and protosalts of iron*, white or yellow precipitates, which are all readily soluble in acids or in ammoniacal salts. Alkaline borates, when fused with metallic oxides, dissolve many of them, forming double salts, which, in many cases, possess characteristic colours: hence borax (acid borate of sodium, BO^3NaH) is of great use as a blowpipe reagent. To detect boric acid before the blowpipe, the substance is powdered, and mixed with from three to four times its volume of a mixture of 1 part fluorspar, and $4\frac{1}{2}$ parts acid sulphate of potassium. This mixture is moistened with water, so as to form a paste, and a little of it taken up on a platinum-wire, and heated in the inner blowpipe flame, when, if boric acid be present, fluoride of boron will be formed, and will communicate a momentary green colour to the outer flame. If boric acid be present in small quantities, very keen observation is necessary to detect it by this method.

(c) The best method for the detection of boric acid either in soluble or insoluble borates, is to mix them with alcohol, to add sulphuric acid little by little, and set fire to the mixture, when the flame of the alcohol will be coloured green. The mixture should be frequently stirred during the combustion. This reaction alone is not absolutely decisive as to the presence of boric acid, since there are other substances, *e. g.* salts of copper, which communicate a similar green colour to the flame of alcohol. Another method is to immerse a strip of yellow turmeric paper into a solution in hydrochloric acid of the substance under examination: when, if even a trace of boric acid be present, the turmeric paper, after being dried, will have a brown colour. When heated with sulphuric and hydrofluoric acids, or (less readily) with sulphuric acid and alcohol, borates are decomposed; in the former case fluoride of boron, in the latter boric ether, being formed. All insoluble native borates are entirely decomposed by fusion with an alkaline carbonate. In a mixture of a borate and a phosphate, the phosphoric acid may be precipitated as phosphate of magnesium and ammonium, while the boric acid remains in solution.

Estimation of Boron.—Stromeyer (Ann. Ch. Pharm. c. 82) states that boron may be estimated as fluoborate of potassium, BF^6K^2. He adds excess of hydrofluoric acid to a solution of borate of potassium, and evaporates to dryness in a platinum or silver vessel. The dry salt is stirred up with a solution of acetate of potassium of 20 p. c., and after some hours thrown on a weighed filter, washed first with the same solution, then with strong alcohol, dried at 100°, and weighed.

11. **Silicon.** Si. Atomic weight, 28·5.

One of the most widely spread elements in the mineral kingdom. It occurs native always in the form of silicic acid, or silica, either free or combined: by far the majority of minerals are silicates of different bases, in which the silica and the metal exist in the most various proportions. It also occurs in the ashes of vegetable and animal substances, and, as soluble silica, in mineral springs. Pure silicon is a dark-brown, heavy powder, which is partially oxidised when heated in contact with air.

OXIDES AND ACIDS OF SILICON. a. *Silicic Anhydride, Silica,* SiO^2.—Silica is found native in two modifications; the crystalline (quartz, rock-crystal) and the amorphous (opal, hyalite, &c.). In chalcedony, agate, and flint, both modifications are present. When artificially prepared, silica is a white amorphous powder, non-volatile at any heat, *absolutely insoluble in water and in all acids, excepting hydrofluoric acid,* more soluble than the crystalline modification in caustic alkalis or alkaline carbonates. It combines with one atom of water, forming

b. *Silicic Acid,* SiO^3H^2.—This is sometimes called soluble silica: it is soluble in all acids, and to a slight extent in water. It is obtained when an aqueous solution of an alkaline silicate is decomposed by an acid, or when fluoride, chloride, or sulphide of silicon is decomposed by water; when it separates as a transparent gelatinous mass. When dried (and more speedily if ignited) it loses its water and becomes insoluble in acids, being in fact converted into silica.

All silicates are insoluble in water, with the exception of those of potassium and sodium. The aqueous solution of an alkaline silicate has an alkaline reaction, and gives with *calcium-, barium-, lead-,* and *silver*-salts a white or yellowish precipitate, soluble in dilute nitric or hydrochloric acid: it is decomposed by a concentrated acid, silicic acid being separated. *Chloride* and *carbonate of ammonium,* and (though less completely), *sulphides of ammonium* and *potassium,* precipitate gelatinous silicic acid from solutions of alkaline silicates: *lime-* or *baryta-water,* a solution of *alumina in potash,* or of *oxide of zinc in ammonia,* precipitate insoluble double silicates. (c) When a concentrated solution of an alkaline silicate is saturated with nitric or hydrochloric acid, gelatinous silicic acid is separated; if the solution be very dilute, the silicic acid remains in solution. When this solution is evaporated to a certain point, the silicic acid separates either as a gelatinous mass or a flaky powder, which, when completely dried in the water-bath, is converted into insoluble silica. If the dry residue (which must not have been ignited) be now treated with water, the alkaline or earthy chlorides or nitrates that have been formed are dissolved out, and pure silica is left. If any of those metals be present whose chlorides or nitrates lose a portion of their acid when evaporated to dryness, and form basic salts insoluble in water (*e. g.* aluminium, iron, magnesium), it is necessary to moisten the dry residue with concentrated hydrochloric acid before treating it with water, and to let it stand for half an hour in the cold: by which process the insoluble basic salts are entirely converted into soluble normal salts, and can be completely dissolved out by water. This is the process adopted for the separation of silica from all bases that are soluble in nitric or hydrochloric acids.

Gelatinous silicic acid, or silica that has not been ignited, is readily and abundantly soluble in caustic alkalis, or alkaline carbonates, especially on the application of heat. Crystalline silica, or amorphous silica after ignition, is less easily soluble in alkalis: but both are readily converted into the soluble modification by fusion (whether free or in combination with bases) with an excess of alkaline carbonate.*

Blowpipe reactions.—Besides its absolute insolubility in all acids except hydrofluoric acid, silica exhibits before the blowpipe some characteristic reactions by which it is easily recognised. (c) When heated with *microcosmic salt* on a platinum wire before the blowpipe, silica is scarcely dissolved at all, but a clear bead is obtained in which the silica is perceptible as a spongy mass. The undissolved silica is more perceptible while the bead is hot than after it has cooled. If pure silica be employed, the bead is quite clear, and not at all opalescent. If a silicate be employed, its base is dissolved by the microcosmic salt, while the silica remains undissolved: but the solution of many metallic bases in microcosmic salt furnishes an opalescent bead, in which the undissolved silica cannot well be discerned. When heated with

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* Owing to the solubility of silica in caustic alkalis or alkaline carbonates, it is impossible in accurate analysis to heat or evaporate solutions containing these substances in glass or porcelain vessels; in such cases platinum vessels must be employed.

borax before the blowpipe, silica is slowly but completely dissolved, a transparent colourless glass being formed. (c) When heated before the blowpipe with *carbonate of sodium*, silica, or a silicate rich in silica, displaces carbonic anhydride, with effervescence, and fuses to a clear glass, which remains transparent on cooling. The alkaline carbonate must not be employed in excess. It is very difficult to obtain this reaction with silicates containing calcium or magnesium. Silica is the only body which exhibits this reaction.

Pure silica leaves no residue when evaporated with excess of hydrofluoric acid. It is also entirely soluble when boiled in a platinum vessel with a solution of caustic alkali or alkaline carbonate; the solution, if saturated, deposits gelatinous silicic acid on cooling. If an earthy or other metal be present, a metallic silicate remains undissolved. These reactions are employed for testing the purity of silica.

Analysis of Silicates.—The different silicates which are found native, or prepared artifically, are either crystalline, or amorphous, transparent, variously coloured bodies (*e. g.* glass); they generally contain a variety of bases, according to the quantity and nature of which the behaviour of different silicates towards decomposing agents varies considerably. Some silicates are entirely decomposed when finely powdered and treated with acids, the whole of the silica being separated as gelatinous silicic acid. To this class belong the *Zeolites*, which are distinguished by their containing a certain quantity of water; the majority of *scoriæ*; and generally those silicates in which the proportion of a strong base greatly exceeds that of the silica. Many silicates (*e. g.* Vesuvian, garnet) require to be ignited or fused before they can be decomposed by acids. Zeolites, when their water has been driven off by ignition, are more difficultly attacked by acids than they are before ignition. There are however some exceptions to this rule; for prehnite, a silicate containing water, is more readily decomposed by acids after than before ignition.

The analysis of those silicates which are completely decomposed by acids is very easily effected. The substance is finely powdered and digested with concentrated hydrochloric acid (at a gentle heat, if necessary), till no gritty particles can be detected by rubbing with a glass rod, and only gelatinous silicic acid remains undissolved. A portion of the silicic acid is dissolved by the hydrochloric acid, to render which insoluble, the mixture is evaporated to complete dryness in the water-bath, with frequent stirring towards the end of the operation: when the residue is completely dry, it is thoroughly moistened with concentrated hydrochloric acid, and allowed to stand for half an hour in the cold, then digested with warm water, the silica filtered off, dried, ignited, and weighed. Moderately dilute sulphuric acid decomposes the majority of silicates more readily than hydrochloric acid; but as the analysis by sulphuric acid of those which contain calcium is attended with considerable difficulty, hydrochloric acid is preferable in such cases. Nitric acid is used in the case of silicates which contain lead.

The majority of silicates, however, cannot be completely decomposed by simple digestion with acids. For the analysis of this class of silicates, the first step is to render them decomposable by hydrochloric acid. This is generally effected as follows: the mineral is reduced to an impalpable powder, by pounding in an agate mortar, (and levigation, if necessary,) and then fused in a platinum crucible with from 3 to 4 times its weight of dry carbonate of sodium, or of a mixture of 2 parts carbonate of potassium, and $1\frac{1}{2}$ part carbonate of sodium. As the heat of a lamp is generally insufficient for this purpose, the platinum crucible is placed in an earthen crucible half filled with carbonate of magnesium, and exposed to a full red heat in the furnace for twenty minutes or half an hour. The platinum crucible, when cold, is placed in a beaker, and the fused mass dissolved by the gradual addition of dilute hydrochloric acid: in order to avoid loss from the violent effervescence caused by the escape of carbonic anhydride, the beaker is covered with a watch-glass or a porcelain basin. Gentle heat is applied to facilitate the decomposition of the fused mass, and then it must be ascertained by rubbing with a glass-rod that there are no gritty particles of undecomposed silicate among the separated silicic acid. From this point the analysis proceeds precisely in the manner detailed above in the case of silicates which are decomposed by acids. The silica is weighed directly, and all the bases, except the alkaline metals, are determined in the filtered solution. The silica must be completely dried before ignition.

Many native silicates, (as zircon, cyanite, cymophane, &c.) are decomposed with difficulty by fusion with alkaline carbonates, a long time and a very strong heat being required. In these cases the decomposition is facilitated by the addition of a fragment of potash or soda, which, however, to avoid injuring the crucible, must be introduced into the middle of the mixture of silicate and carbonate, which has been solidly pressed down into the crucible.

It is obvious that fusion with alkaline carbonates is inadmissible for the determination of the alkaline metals contained in silicates. For this purpose carbonate of barium, or caustic baryta, must be substituted for the alkaline carbonates. In this case the decomposition is more difficult. The silicate and its flux must be mixed together most intimately, and a longer time is required for the fusion. The silica is separated in the same manner as in the former case: the barium is then removed from the acid solution by the careful addition of sulphuric acid, and the other bases estimated in the filtrate. Or the silica and all the bases except the alkaline metals may be estimated by fusion with alkaline carbonates, and the alkaline metals estimated in another portion of the mineral by decomposing it by hydrofluoric acid. For this purpose the mineral is finely powdered, moistened with dilute sulphuric acid in a platinum crucible, and placed in a leaden vessel covered with a lid, at the bottom of which is a quantity of powdered fluorspar covered with concentrated sulphuric acid. Gentle heat is applied, and the silicate is exposed to the vapours of hydrofluoric acid for one or two days. All the silica is thus volatilised as fluoride of silicon, and a clear solution obtained containing sulphates of all the metals contained in the silicate. This is treated with sulphuric acid, evaporated to dryness, and the alkaline metals determined in the residue in the usual way.

Many minerals (as clinkstone, clayslate, &c.) contain a mixture of both classes of silicates, and so may be partially, but not completely, decomposed by acids. These are digested in concentrated hydrochloric acid, diluted with water, and filtered, when the filtrate contains the bases of the decomposable silicates. The separated silicic acid, together with the undecomposed silicates, is then repeatedly boiled with fresh portions of a strong solution of carbonate of potassium, and filtered hot. The alkaline solution contains all the silicic acid of the decomposable silicates, which is separated as silica by evaporation to dryness with hydrochloric acid. The insoluble residue is then analysed by the methods described for the analysis of silicates undecomposable by acids.

In some silicates there are other constituents to be estimated besides water, silica, and metallic bases. Thus, tourmaline contains fluorine and boric acid; nosean, chlorine and sulphuric acid; cancrinite, carbonic acid; haüyne and ultramarine, chlorine and sulphur; and many minerals contain phosphoric acid. Tourmaline cannot be decomposed by hydrofluoric acid till it has been ignited and all its fluorine driven off as fluoride of silicon.

Silica is separated from *titanic acid* by fusion in a platinum crucible with acid sulphate of potassium, and subsequent treatment with water, which dissolves out the titanic acid, while the silica remains undissolved.

c. *Fluosilicic Acid*, SiF^6H^2.—When fluoride of silicon is conducted into water it is partially decomposed, silicic acid being separated, while fluosilicic acid remains in solution ($3SiF^4 + 3OH^2 = 2SiF^6H^2 + SiO^3H^2$). Fluosilicic acid is a colourless liquid, having an acid reaction: when evaporated in a platinum vessel it volatilises entirely, being decomposed into fluoride of silicon and hydrofluoric acid. If the free acid, or a fluosilicate mixed with hydrochloric acid, be evaporated in glass vessels, the hydrofluoric acid set free attacks the glass. Fluosilicates are mostly soluble in water, and are decomposed by acids and alkalis. With *sodium-potassium-*, *lithium-*, and *barium*-salts, they give a gelatinous precipitate, which separates entirely on the addition of alcohol. (This precipitation of barium by fluosilicic acid affords the best method for separating barium from strontium.) Fluosilicates are all decomposed by heat, fluoride of silicon being given off, while a metallic fluoride is left.

Boron forms with fluorine a compound analogous to fluosilicic acid. The reactions of fluoboric acid closely resemble those of fluosilicic.

12. **Phosphorus.** P. Atomic weight, 31.

Phosphorus occurs very abundantly both in the mineral and the organic kingdom, almost exclusively in the form of metallic phosphates. At least two different modifications of it are known ; viz. *Ordinary*, and *Amorphous* phosphorus. Ordinary phosphorus is a yellowish-white opaque solid, whose structure is really, though not apparently, crystalline : it melts at about 44°, and volatilises between 250° and 300°. It is insoluble in water, very slightly soluble in alcohol and ether, readily soluble in bisulphide of carbon. It emits light in the dark at ordinary temperatures. It is very readily oxidised by all oxidising agents, forming phosphoric and phosphorous anhydrides : in contact with the air it takes fire on a very slight elevation of temperature, or even by friction, and burns with a brilliant flame, forming dense white fumes, principally of phosphoric anhydride. When heated in an atmosphere free from oxygen, it passes into the *amorphous* modification. This is a dark red powder, which is insoluble in bisulphide of carbon. It is a much less active body than the ordinary phosphorus, and may be heated in contact with air to considerably above 200° without taking fire. At about 260°, it is reconverted into ordinary phosphorus. In the decomposition of many compounds containing phosphorus, the element frequently separates in this modification.

ACIDS AND OXIDES OF PHOSPHORUS. a. *Phosphide of Hydrogen*, (phosphuretted hydrogen), PH^3. *Metallic Phosphides.*—Phosphorus combines with hydrogen and several other metals, forming metallic phosphides. Phosphide of hydrogen is a colourless gas, with a peculiar smell resembling that of garlic ; slightly soluble in water. It is readily inflammable : and sometimes, when it contains a lower phosphide of hydrogen, it takes fire spontaneously in contact with the air. It is entirely absorbed by a solution of a *gold*- or *silver*-salt, producing a dark precipitate of reduced metal, phosphoric acid being formed simultaneously. With *lead*- and *copper*-salts it gives a black, with *chloride of mercury*, a yellow, precipitate, consisting chiefly of metallic phosphide.

b. *Phosphoric Anhydride*, P^2O^5.—Formed by the complete and rapid combustion of phosphorus in dry air or oxygen. A white flaky powder, readily soluble in water and alcohol. It is one of the most hygroscopic substances known, rapidly absorbing moisture from the air and being converted into metaphosphoric acid: hence it is frequently employed for drying gases.

c. *Ordinary or Tribasic Phosphoric Acid*, PO^4H^3.—Ordinary phosphoric acid forms colourless crystals, or a syrupy fluid, which, at a high temperature, loses the elements of water, and is converted wholly or partially into metaphosphoric acid, PO^3H. When heated to redness in an open platinum vessel it volatilises entirely without leaving any residue: in a glass or porcelain vessel a residue is left, since phosphoric acid partially decomposes silicates. Phosphoric acid is readily soluble in water and alcohol. Its solution has a strong acid reaction, and gives no precipitate with a solution of *albumen* or of *chloride of barium:* with excess of *lime-* or *baryta-water* it gives a white precipitate.

Phosphoric acid, being tribasic, forms three classes of salts, according as one, two, or three atoms of basic hydrogen are replaced by metals. There are the *Biacid Phosphates* (PO^4NaH^2), the *Monacid* (PO^4Na^2H), and the *Normal Phosphates* (PO^4Na^3). Only the alkaline phosphates are soluble in water; the solution has an alkaline reaction: all others are difficultly soluble or insoluble in water, readily soluble in nitric or hydrochloric acids. The alkaline-earthy phosphates, when freshly precipitated, are soluble in acetic acid. When the solution of an alkaline-earthy phosphate in an acid is neutralised by an alkali, the original phosphate is precipitated unchanged, and is not soluble in excess of alkali. The insoluble phosphates which are precipitated from metallic solutions by phosphate of sodium, are generally soluble in excess of the solution from which they are precipitated; when this solution is heated a precipitate is produced, which redissolves on cooling.

With *nitrate of silver* soluble phosphates give a yellow precipitate of PO^4Ag^3, soluble in nitric acid and ammonia. With *acetate of lead*, they give a white precipitate of PO^4Pb^3, insoluble in ammonia and acetic acid, soluble in nitric acid. If a chloride be present, the precipitate contains chloride of lead chemically combined with it. (c) When fused before the blowpipe, phosphate of lead forms a crystalline bead on cooling. With *chlorides of barium* and *calcium*, they give white precipitates of PO^4Ba^2H, and PO^4Ca^2H, readily soluble in nitric, hydrochloric, phosphoric, and acetic acids. Phosphate of calcium separates from its acetic acid solution, after some time (especially if heated), in a crystalline form. It is also somewhat soluble in water containing carbonic acid; and in ammoniacal salts, even in presence of free ammonia. From its acetic acid solution (or from its hydrochloric acid solution after addition of sufficient acetate of sodium) the whole of the calcium may be precipitated as oxalate by oxalate of ammonium. From its hydrochloric or nitric acid solution, the addition of sulphuric acid and alcohol removes the whole of the calcium as sulphate. (These methods are employed for the estimation of lime in the ashes of plants, and in bone-earth.) (c) With *sulphate* or *chloride of magnesium*, to which ammonia and chloride of ammonium have been added*, they give a white crystalline precipitate of $PO^4Mg^2NH^4 + 6H^2O$, readily soluble in all acids, slightly soluble in pure water, absolutely insoluble in water containing free ammonia, even in presence of excess of ammoniacal salts. In very dilute solutions the precipitate forms very slowly; its deposition is accelerated by scratching, with a glass rod, the inside of the vessel containing the solution. This precipitate, which by ignition is converted into $P^2O^7Mg^4$ ($2PO^4Mg^2NH^4 = P^2O^7Mg^4 + 2NH^3 + OH^2$), serves for the detection and estimation of phosphoric acid (in absence of arsenic acid) in all compounds which are soluble in water, and whose aqueous solution is not precipitated by ammonia and chloride of ammonium. If tartaric acid and a sesquisalt of iron be present, the precipitate is likely to contain a little tartrate of magnesium and sesquioxide of iron.

With *sesquichloride of iron*, they give a yellowish-white precipitate of sesquiphosphate, PO^4Fe^2, soluble in hydrochloric acid, excess of sesquichloride, in sesquiacetate of iron, and in ammonia. This precipitate is absolutely insoluble in acetic acid; it therefore forms when acetate of sodium is added to its solution in hydrochloric acid, or when acetate of sodium and *a little* sesquichloride of iron are added to the hydrochloric acid solution of an alkaline-earthy phosphate. When the hydrochloric acid solution of any phosphate (the free acid, if any, having been first neutralised with ammonia or carbonate of ammonium) is treated with acetate of sodium and a slight excess of sesquichloride of iron (just enough to give a red tinge to the solution), and the mixture heated to boiling, a reddish-brown precipitate is formed, which contains *all* the phosphoric acid and *all* the sesquioxide of iron: it must be filtered hot, and washed with hot water. Arsenic acid exhibits this reaction as well as phosphoric acid; and sesquisalts of aluminium are precipitated under the same circumstances, though not so completely as sesquisalts of iron. On this reaction is based an accurate method for the estimation of phosphoric acid by means of a known volume of a standard solution of sesquichloride of iron; as well as for the complete removal of phosphoric acid and of iron from a solution in which calcium, magnesium, manganese, and other isomorphous metals, have to be estimated. *Sesquinitrate of uranium* behaves with soluble phosphates exactly like sesquisalts of iron. *Subnitrate of mercury* gives, with soluble phosphates, a white precipitate, readily soluble in nitric acid. If the solution of any phosphate in excess of nitric acid is evaporated in the water-bath to complete dryness, with excess of metallic mercury, and the dry residue (which contains no free acid) treated with water, all the metals contained in the phosphates are dissolved as nitrates, while the whole of the phosphoric acid remains undissolved as subphosphate of mercury. This reaction is employed by H. Rose for the separation of phosphoric acid from all metals, excepting aluminium. The insoluble portion is freed from mercury by gentle ignition with an alkaline carbonate, and the phosphoric acid estimated in it as phosphate of magnesium and ammonium: the mercury is removed from the soluble portion by hydrochloric acid and ammonia, or by evaporation and gentle ignition. If a sesquisalt of iron be present, the iron is found partly in the soluble, partly in the insoluble portion. If the nitric acid solution of the phosphates of the alkaline or alkaline-earthy metals, or of magnesium, be evaporated to dryness with a solution of sesquinitrate of iron, which contains, at least, enough iron to combine with all the phosphoric acid present, and the residue heated to 180°, until it ceases to give off nitrous fumes, all the above-named bases are converted into soluble nitrates, while all the iron remains as insoluble sesquiphosphate. The nitric acid solution must be entirely free from hydrochloric or sulphuric acid. A sesquisalt of aluminium may be substituted for the sesquisalt of iron; but in this case the separation is less complete.

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* Add ammonia to the magnesium solution; dissolve the precipitated hydrate of magnesium in hydrochloric acid, and then add excess of ammonia: no precipitate is formed, since hydrate of magnesium is soluble in ammoniacal salts.

(c) The best reagent for the detection of very small traces of phosphoric acid is *molybdate of ammonium*. If the solution of a phosphate be added to excess of a solution of this reagent, free nitric acid added, and the whole heated, the solution immediately assumes a yellow colour, and a bright yellow precipitate of phosphate and molybdate of ammonium is formed, either immediately or after some time. This precipitate is insoluble in acids, soluble in ammonia, or in excess of the phosphate; hence this reaction is peculiarly fitted for the detection of very small traces of phosphoric acid (as in minerals, soils, or the deposits from mineral springs). Arsenic acid exhibits the same reaction.

Normal phosphates of fixed bases are not at all decomposed by ignition, biacid phosphates are converted by ignition into metaphosphates, monacid phosphates into a mixture of normal phosphate and metaphosphate (pyrophosphate). The alkaline-earthy phosphates are only partially decomposed by fusion with an alkaline carbonate, while most other insoluble phosphates (*e. g.* phosphates of magnesium, zinc, copper, protophosphate of manganese, sesquiphosphate of iron) are completely decomposed by this means; the fused mass always contains tribasic phosphoric acid. By boiling in a solution of caustic alkali or of alkaline carbonate, the insoluble phosphates are only partially, or not at all, decomposed. Phosphate of aluminium can only be completely decomposed by fusion with its own weight of silica, and six times its weight of carbonate of sodium; the fused mass is then dissolved in water, the silicic acid precipitated by carbonate of ammonium and filtered off, the filtrate acidulated with hydrochloric acid and saturated with ammonia, and the phosphoric acid precipitated from it by a salt of magnesium.

Separation and estimation of Phosphoric Acid.—When the hydrochloric acid solution of sesquiphosphate of iron, phosphate of aluminium, magnesium, &c., is digested with excess of carbonate of barium, the whole of the phosphoric acid is removed; if any sesquisalts be present, their metals are precipitated at the same time as sesquihydrates. Phosphoric acid may be completely separated from barium, strontium, and lead, by sulphuric acid; from calcium, by sulphuric acid and alcohol. Phosphate of lead, suspended in water, is completely decomposed by hydrosulphuric acid, sesquiphosphate of iron by sulphide of ammonium; all the phosphoric acid is contained in the filtrate. For the accurate separation of phosphoric acid from an excess of sesquisalt of iron (even in presence of calcium and magnesium), the substance is dissolved in hydrochloric acid, and the solution heated to boiling with sulphite of sodium, until all the sesquisalt of iron is converted into protosalt; the excess of sulphurous acid is then driven off by boiling, the solution neutralised with carbonate of sodium, a very little chlorine-water added in order to reconvert a small quantity of the iron into sesquisalt, then an excess of acetate of sodium, when, if the least trace of phosphoric acid be present, a white precipitate of sesquiphosphate of iron is formed. Chlorine-water is then again added, drop by drop, until the solution assumes a red tinge, the whole heated to boiling, and filtered. The precipitate, which contains all the phosphoric acid, is either decomposed by sulphide of ammonium, or dissolved in hydrochloric acid, heated with sulphite of sodium, excess of caustic soda added, and the whole boiled till the precipitate is converted into black ferroso-ferric oxide; in either case the phosphoric acid is determined in the filtrate as phosphate of magnesium and ammonium (p. 205). For the separation of phosphoric acid from aluminium the compound is dissolved in caustic soda, and the phosphoric acid precipitated from the dilute solution by chloride of barium or baryta-water as phosphate of barium, fresh portions of caustic soda and carbonate of sodium being added at the same time, and the whole heated nearly to boiling ; all the aluminium is then contained in the filtrate. The phosphate of barium is dissolved in hydrochloric acid, the barium precipitated by sulphuric acid, and the phosphoric acid determined in the filtrate as phosphate of magnesium and ammonium. If a sesquisalt of iron be also present, it is reduced, as above, by sulphite of sodium, before the treatment with caustic soda.*

Phosphoric acid is readily distinguished from sulphuric acid by the solubility in acids of its barium-salt. For its detection in *neutral* or *alkaline* solutions, *chloride of ammonium*, *ammonia*, and a *magnesium*-salt, are generally employed ; in an *acid* solution, *sesquichloride of iron*, and *acetate of sodium*. The most delicate reagent of all is *molybdate of ammonium*. Since arsenic acid exactly resembles phosphoric acid in all these reactions, the absence of this acid must previously be ascertained. Arsenic acid is readily distinguished from phosphoric acid, and if present, may be entirely removed by passing hydrosulphuric acid into the warm acid solution (p. 84).

d. *Metaphosphoric Acid*, PO^3H (monobasic). — When phosphoric anhydride is dissolved in water, an acid solution is obtained, which differs in many of its reactions from that of phosphoric acid. It is metaphosphoric acid, PO^3H. Its salts are also obtained by the ignition of the corresponding biacid phosphates. The following are the principal reactions which distinguish it from phosphoric acid. With *albumen* it gives an abundant white precipitate; with *chloride of barium*, an abundant white precipitate, soluble with difficulty in a large excess of the acid ; with *nitrate of silver*, a white precipitate, soluble in excess of metaphosphoric acid. With *molybdate of ammonium*, it gives no precipitate or coloration, until, by the action of the free nitric acid present, it has been partly converted into phosphoric acid. A solution of metaphosphoric acid is very slowly converted into phosphoric acid in the cold ; the conversion is facilitated by heat. All metaphosphates are converted into phosphates by heating with a concentrated acid, or by fusion with an alkaline carbonate.

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* When alkaline liquids are boiled in glass or porcelain vessels, sensible quantities of silicic acid are always dissolved : hence, in very accurate analyses, platinum vessels must be employed.

Blowpipe reactions.— When metaphosphate of sodium, or the glacial acid, is fused on charcoal before the blowpipe, and a piece of metallic zinc introduced into the fluid mass, a partial reduction of the acid takes place, and the liberated phosphorus burns with a brilliant flame.

e. *Pyrophosphoric Acid*, $P^2O^7H^4$ (quadribasic). — Phosphoric and metaphosphoric acids are capable of combining together in several proportions, forming compounds which, owing to their exhibiting peculiar reactions in some cases, have sometimes been regarded as distinct acids. The compound formed by the combination of 1 atom of each of these acids ($PO^4H^3+PO^3H=P^2O^7H^4$) has thus been called *pyrophosphoric acid.* This compound is produced by heating phosphoric acid to 213°, and its salts are obtained by igniting the corresponding monacid phosphates. It is soluble in water. Its solution does not precipitate *albumen* or *chloride of barium.* Its alkaline salts are soluble in water, with an alkaline reaction; its other salts are soluble in acids, and generally in an excess of phosphate of sodium, forming soluble double salts which exhibit a peculiar behaviour with reagents. Thus, from a solution of sesquiphosphate of iron, or protophosphate of manganese, in pyrophosphate of sodium, the heavy metal can scarcely be precipitated by hydrosulphuric acid or sulphide of ammonium. This peculiarity of behaviour is found in several other polybasic acids. The insoluble pyrophosphates, like the corresponding phosphates, are soluble in excess of the metallic salts from which they are precipitated, and the solution is reprecipitated by heat; but this precipitate is *not* redissolved on cooling. The alkaline-earthy pyrophosphates are difficultly soluble in acetic acid. With *nitrate of silver* pyrophosphate of sodium gives a white precipitate, almost insoluble in excess of pyrophosphate, soluble in nitric acid and ammonia. The same methods by which metaphosphates are converted into phosphates, apply equally to pyrophosphates.

Besides pyrophosphoric acid, other acids have been described by Fleitmann and Henneberg (Ann. Ch. Pharm. lxv. lxxii.), which are probably combinations in different proportions of phosphoric and metaphosphoric acid. Among these are $2P^2O^5, 3H^2O, =PO^4H^3+3PO^3H$: $5P^2O^5, 6H^2O=PO^4H^3+9PO^3H$, &c. The same chemists have also obtained a series of salts, which they regard as polymeric modifications of metaphosphates, from which they differ in several properties. But the formulæ which they assign to these salts always contain variable quantities of water of crystallisation; and, if this water be in each case introduced into the formula of the salt, it will be found that these salts too may be regarded as compounds of phosphates and metaphosphates in different proportions.

f. *Phosphorous Anhydride*, P^2O^3. — Formed by the slow and imperfect combustion of phosphorus; as when phosphorus is oxidised by exposure to the air at the ordinary temperature. A white powder, smelling like garlic. It is readily soluble in water, forming

g. *Phosphorous Acid*, PHO^3H^2 (bibasic). — A syrupy liquid, which cannot be crystallised without great difficulty. It is entirely decomposed by heat, phosphoric acid being formed, and phosphide of hydrogen evolved ($4PO^3H^3=3PO^4H^3+PH^3$).

The normal alkaline phosphites are soluble in water; all others are difficultly soluble or insoluble. When treated with oxidising agents, as chlorine or nitric acid, phosphites are converted into phosphates. With *chlorides of barium and calcium*, alkaline phosphites give a white precipitate, soluble in acetic and free phosphorous acids; with *acetate of lead*, a white precipitate of phosphite of lead, insoluble in acetic acid. This is the least soluble of all the phosphites. With *magnesium*-salts, a dilute solution of a phosphite gives no precipitate. Phosphorous acid is a powerful reducing agent, precipitating the metals from solutions of salts of gold and silver, and subsalts of mercury; the reduction is much facilitated by saturating the acid with ammonia. With *chloride of mercury* it gives a white precipitate of subchloride, $ClHg^2$; if the mercury salt be in excess, the reduction does not proceed further; but, if the phosphorous acid be in excess, metallic mercury is reduced, especially on the application of heat. When heated with *sulphurous acid*, phosphorous acid gives phosphoric and hydrosulphuric acids ($3PO^3H^3+SO^3H^2=3PO^4H^3+SH^2$); and, if the sulphurous acid be in excess, the hydrosulphuric acid is decomposed and sulphur separated (p. 21). If the phosphorous acid contain any arsenic, it is entirely precipitated as sulphide. Arsenic acid is reduced by phosphorous acid to arsenious acid, which, by fusion with phosphorous acid, is reduced to metallic arsenic, which separates as a dark brown powder. Phosphorous acid dissolves zinc and iron, with evolution of phosphide of hydrogen. Dry phosphites are decomposed by heat, hydrogen being evolved, and a pyrophosphate formed; the normal phosphite of lead, and one or two others, evolve phosphide of hydrogen as well as hydrogen.

h. *Hypophosphorous Acid*, PH^2O^2H (monobasic).—Formed, together with phosphoric acid and phosphide of hydrogen, when phosphorus is boiled in a solution of caustic alkali or alkaline-earth. The acid is isolated by decomposing its barium-salt by sulphuric acid. It is a syrupy fluid, very similar in appearance to phosphorous acid. By heat it is decomposed into phosphoric acid and phosphide of hydrogen ($2PO^2H^3 = PO^4H^3 + PH^3$). All hypophosphites are soluble in water. Hypophosphorous acid is even a more powerful reducing agent than phosphorous acid. With *nitrate of silver* it gives a white precipitate, which blackens speedily even in the cold: with *acetate of lead*, *lime-*, and *baryta-water*, no precipitate. All hypophosphites are decomposed by heat, phosphide of hydrogen being evolved, and a pyrophosphate or acid phosphate left behind. With *copper*-salts, hypophosphorous acid separates in the cold a reddish yellow precipitate of subhydride of copper, Cu^2H, which on heating is decomposed into metallic copper and hydrogen.

Determination of phosphorus in organic compounds. Organic compounds containing phosphorus are fused with carbonate and nitrate (or chlorate) of potassium, by which means the phosphorus is converted into phosphoric acid, and may be estimated as phosphate of magnesium and ammonium.

13. **Organic Acids.**

Of the numerous acids containing carbon, oxygen, and hydrogen (and occasionally nitrogen), commonly called *organic acids,* a few are of sufficient importance as reagents in mineral analysis to make it necessary to enumerate their reactions. A general reaction, common to nearly all these acids, is, that their alkaline and alkaline-earthy salts are converted by ignition into carbonates, with separation of carbon and consequent blackening of the compound. Oxalates, if perfectly pure, are not blackened by ignition.

The organic acids which we are about to mention may be conveniently divided into two classes: *volatile* and *non-volatile* acids. The volatile acids, when heated in the free state, are volatilised entirely, generally without decomposition, and if pure, leave no carbonaceous residue: they may be removed from their salts by distillation with dilute sulphuric acid. The non-volatile acids are decomposed when heated in the free state, a considerable carbonaceous residue being left: they cannot be removed from their salts by distillation with dilute sulphuric acid. The non-volatile acids are further distinguished from the volatile by the property of hindering the precipitation by alkalis of certain metallic oxides from their salts (*e. g.* sesquioxide of iron): for the non-volatile acids, being polybasic, form double salts of the alkaline and the heavy metal, which are soluble in water. Volatile organic acids do not hinder this precipitation. In presence of non-volatile organic acids, the heavy metal may be precipitated as sulphide by sulphide of ammonium.

VOLATILE ORGANIC ACIDS. a. *Acetic Acid*, $C^2H^3O^2H$.—Below 17°, acetic acid forms a white crystalline mass; above that temperature, a colourless fluid, with an irritating smell, which is familiar to every one as that of vinegar. All acetates are soluble in water: the least soluble are acetate of silver and subacetate of mercury, whence acetic acid produces crystalline precipitates in not too dilute solutions of salts of silver and subsalts of mercury. Most acetates (especially those which contain a strong base) are decomposed by heat, *acetone* being formed, the vapour of which is combustible and has a characteristic smell ($2C^2H^3O^2K = C^3H^6O + CO^3K^2$). With *sesquisalts of iron*, a solution of an acetate (not free acetic acid) gives a dark-red colour, which is destroyed by mineral acids, not by excess of acetic acid. Excess of ammonia precipitates all the iron from this solution as sesquihydrate: when the solution is heated, all the iron is precipitated as basic acetate. (c) When a dry acetate (or a concentrated aqueous solution) is heated with excess of sulphuric acid and a little alcohol, acetic ether or acetate of ethyl ($C^2H^3O^2C^2H^5$) is formed, and easily recognised by its peculiar fragrant smell. If too much alcohol be taken ether will be formed, the smell of which will mask that of the acetic ether. When a dry acetate is heated with arsenious acid, *kakodyl*, ($(C^2H^3)^4As^2$) is formed, which possesses a most nauseous and characteristic smell. This reaction does not distinguish acetic acid from propylic ($C^3H^5O^2H$) and other higher acids of the series, which form, with arsenious acid, compounds which closely resemble kakodyl in smell. For the detection of acetic acid in a solution containing an acetate together with other compounds, the best method is to distil the solution with dilute sulphuric acid, by which the acetic acid is set free, and, being volatile, passes over, and is found in the distillate. A very dilute acid solution should be neutralised with carbonate of sodium, and concentrated by evaporation, previous to distillation. For the detection of acetic acid in presence of other volatile acids homologous* to acetic, the aqueous solution of the free acids is *partially* neutralised with potash, and the whole submitted to distillation; when the acetic acid is found, either wholly or partially, in the residue, as acid acetate of potassium, while the other volatile acids (which do not form acid salts with metals), pass over and are found in the distillate. This method of fractional saturation may be applied to the separation of other acids of this series. The boiling-point of each acid in the series rises about 19° for each addition of CH^2; so that a lower acid is always more volatile than the higher ones: and when a mixture of two or more such acids is partially saturated with a base, the higher acid is always completely neutralised before those below it combine with any of the base. Hence, if a mixture of propylic and butyric acids be partially saturated with potash, and submitted to distillation, the lower acid (propylic) being free, will distil over; and if just enough potash has been added to exactly neutralise the butyric acid, the whole of this acid will be found in the residue, and the whole of the propylic in the distillate. If less potash than this has been added, the propylic acid, being more volatile, will pass over first, and then the free butyric acid, while the residue will contain nothing but butyrate of potassium: if more potash has been added, the distillate will contain only propylic acid, the residue a mixture of propylate and butyrate of potassium. Acetic acid is, as has been observed, an exception to this rule: for it forms an acid potassium-salt, which will always be found in the residue.

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* The term *homologous*, suggested by Gerhardt, is applied to those bodies which resemble each other in their chemical properties, and only differ in their composition by CH^2, or some multiple of CH^2. Thus, acetic acid, $C^2H^3O^2H$ propylic acid, $C^3H^5O^2H$, butyric acid, $C^4H^7O^2H$, valerianic acid, $C^5H^9O^2H$, &c. are homologous to each other. Similarly we have series of homologous alcohols, aldehydes, &c.

When an acetate is heated with strong sulphuric acid, acetic acid is given off (with its peculiar smell), and there is no blackening of the mixture.

b. *Formic Acid*, CHO^2H.—Formic acid is a colourless liquid, which boils at 100°; it has a smell somewhat similar to that of acetic acid. All formates are soluble in water, though less so than the corresponding acetates. All formates are decomposed by heat: the fixed alkaline, and alkaline-earthy formates, give off carbonic oxide, leaving a mixed residue of carbonate and free carbon; those of other metals (*e.g.* copper, lead) give off carbonic oxide and anhydride, and leave a residue of reduced metal. Formates exactly resemble acetates in their behaviour with sesqui-salts of iron. Formic acid is, however, easily distinguished from acetic acid, by its property of reducing many metals from their salts, with evolution of carbonic anhydride. Formic acid, or any formate, when heated with *nitrate of silver* or *terchloride of gold*, gives a brown precipitate of metallic silver or gold; with *subnitrate of mercury*, a grey precipitate of metallic mercury; with *chloride of mercury*, a white precipitate of subchloride, which by long boiling is slowly reduced to metallic mercury. They also destroy the colour of *permanganate of potassium*. This reducing action distinguishes formic acid from most of its homologous acids, and renders its detection very easy. For the detection of small quantities of formic acid in solutions which contain other organic compounds, distillation with dilute sulphuric acid is employed: the distillate is saturated with carbonate of sodium, concentrated by evaporation, and the formic acid detected in it by the above reactions. When heated with concentrated sulphuric acid, formic acid and formates are decomposed with effervescence into water and carbonic oxide which burns with a blue flame ($CHO^2H = CO + OH^2$): there is no blackening of the mixture.

c. *Benzoic Acid*, $C^7H^5O^2H$.—Forms white crystals, which when heated, sublime entirely into long needles, leaving only the slightest possible residue of carbon: its vapours are very irritating, and excite coughing. It is very slightly soluble in cold water or acids; hence, when a mineral acid is added to a solution of benzoate, a white precipitate of benzoic acid is produced. Protobenzoates are mostly soluble in water: sesquibenzoates are insoluble. When benzoic acid is added to *sesquichloride of iron*, a yellow precipitate of sesquibenzoate of iron is formed; if the free acid be saturated with ammonia, this precipitate contains the whole of the iron. Hence, benzoate of ammonium is employed as a reagent for separating the sesquioxides from a solution containing proto- and sesquisalts. The metal may be removed from the precipitate by hydrochloric acid, which leaves the benzoic acid undissolved; or the benzoic acid may be removed by ammonia, which leaves sesquihydrate of iron. With *acetate of lead* benzoic acid gives no precipitate: and only a very slight one when the free acid is neutralised with ammonia. (c) When benzoate of calcium is distilled with excess of *lime*, the benzoic acid is decomposed into carbonic anhydride and benzine, C^6H^6, a fragrant oily liquid, insoluble in water, boiling at 80°. The test is thus conducted:—The benzoic acid precipitated by an acid from a soluble benzoate is collected on a filter, dried with blotting-paper, and dissolved in as little lime-water as possible; an equal bulk of lime-water is then added, and the whole distilled. Very small quantities of benzoic acid may be detected in this way. When benzoic acid is heated with strong sulphuric acid, no sulphurous anhydride is evolved, and the mixture is not blackened.

d. *Succinic Acid*, $C^4H^4O^4H^2$ (bibasic).—A homologue of oxalic acid, $C^2O^4H^2$. It forms white crystals, which sublime when heated, leaving a larger residue of carbon than is left in the case of most other volatile organic acids. It is much more soluble in water than benzoic acid, and therefore is not precipitated from its soluble salts by a mineral acid. Protosuccinates are all soluble in water; sesquisuccinates are mostly insoluble. Succinic acid precisely resembles benzoic in its behaviour to sesquisalts of iron: but, as the precipitate of sesquisuccinate is much less voluminous than that of sesquibenzoate, succinate of ammonium is a more convenient reagent than benzoate for the precipitation of sesquisalts. With *acetate of lead* succinic acid gives a precipitate of succinate of lead, soluble in excess of either reagent. With *chloride of barium* it gives no precipitate; but on the addition of ammonia and alcohol, a white precipitate is formed: benzoic acid does not exhibit this reaction. When succinic acid is heated with strong sulphuric acid, the mixture gradually blackens, and sulphurous anhydride is evolved.

NON-VOLATILE ORGANIC ACIDS. a. *Oxalic Acid*, $C^2O^4H^2$ (bibasic).—Forms white crystals, which contain 2 atoms of water of crystallisation: soluble in water and alcohol, giving a strongly acid solution. It is a violent poison. When heated it is almost entirely decomposed, carbonic oxide and anhydride, and some formic acid being formed. The alkaline oxalates are soluble in water, but not very readily, the acid salts less so than the normal; most other oxalates are insoluble. Sesquioxalates are generally soluble. With *calcium*-salts, oxalic acid or a soluble oxalate gives a white crystalline precipitate of normal oxalate of calcium, insoluble in ammonia, ammoniacal salts, and acetic acid, slightly soluble in free oxalic acid, soluble in mineral acids. This precipitate is formed in very dilute solutions, even in sulphate of calcium. This reaction affords the best test both for oxalic acid and for calcium. With soluble *copper*-salts, it gives a precipitate of oxalate of copper: crystallised oxalic acid is not dissolved in a solution of chloride of copper, but is gradually converted into oxalate of copper. In other metallic solutions this change first takes place on the application of heat. With *nitrate of silver* it gives a white precipitate, soluble in nitric acid and ammonia.

When heated with *terchloride of gold*, oxalic acid reduces metallic gold, with evolution of carbonic anhydride. It does not reduce platinum from its salts. When heated with sulphuric acid, all oxalates are decomposed into equal volumes of carbonic oxide and anhydride, and the mixture does not blacken ($C^2O^4H^2 = CO + CO^2 + OH^2$). All oxalates are decomposed by ignition, in manners varying according to the bases which they contain. Oxalates of such metals as form stable carbonates give off carbonic oxide, while a metallic carbonate remains. Those of the metals which do not form carbonates, or whose carbonates are decomposed by ignition, evolve equal volumes of carbonic oxide and anhydride, leaving a residue of metallic oxide. Those of the metals whose oxides are reduced by carbonic oxide, evolve carbonic anhydride alone, and leave a residue of reduced metal.

Since oxalic acid cannot be separated from its salts by distillation with dilute sulphuric acid (for by this treatment it is decomposed into CO and CO^2) it must be classed among the non-volatile acids. But it does not exhibit the reaction which we have already mentioned as generally characteristic of this class of organic acids, that of hindering the precipitation by alkalis of certain metallic oxides. A sesquisalt of iron to which oxalic acid has been added, is completely precipitated by ammonia: but if a fixed alkaline carbonate be employed instead of ammonia, oxalic acid does to a certain extent prevent the precipitation.

b. *Tartaric Acid*, $C^4H^4O^6H^2$ (bibasic).—Forms colourless crystals, very soluble in water: they are decomposed by heat, giving off a peculiar smell, much resembling that of burnt sugar, and leaving a large residue of carbon. Of the alkaline tartrates, the acid salts are much less soluble than the normal: hence, if tartaric acid be added in excess to a solution of *potash*, a white crystalline precipitate of acid tartrate of potassium is formed, which is insoluble in all organic acids except oxalic, soluble in mineral acids, alkalis, and alkaline carbonates: by the two latter solvents it is converted into the soluble normal tartrate, whence the acid tartrate is reprecipitated by acetic acid. As the acid tartrate is soluble in alkalis, potash should not be used for the detection of small quantities of tartaric acid: it is better to employ chloride or nitrate of potassium, in excess of which the acid tartrate is insoluble. Of the other tartrates, the acid salts are more soluble than the normal. (c) With *lime-water* in excess tartaric acid gives a white precipitate of normal tartrate; *chloride of calcium* gives the same precipitate with a normal tartrate; *sulphate of calcium* does not. This precipitate is soluble in acids, even in free tartaric acid, and in ammoniacal salts, but not in ammonia. It is soluble in potash in the cold, but is reprecipitated on boiling the solution, and redissolved on cooling. It is insoluble in chloride of copper. From *nitrate of silver* normal tartrate of potassium reduces metallic silver on heating. All tartrates, when heated with strong sulphuric acid, give off sulphurous anhydride and the mixture is blackened.

Racemic Acid is isomeric with tartaric acid, which it resembles closely in all its reactions. Racemate of *calcium*, however, is insoluble in ammoniacal salts; and is formed, after a time, by racemic acid in a solution of sulphate of calcium. From this reaction racemic might be confounded with oxalic acid: but they are readily distinguished by their behaviour when heated with sulphuric acid, when racemic behaves exactly like tartaric acid.

c. *Citric Acid*, $C^6H^5O^7H^3$ (tribasic).—Forms white crystals, soluble in water and alcohol; they are decomposed by heat, giving off irritating vapours, and leaving a carbonaceous residue less abundant than in the case of tartaric acid. Most citrates are soluble in water. With *potassium*-salts, citric acid gives no precipitate. With *lime-water*, citric acid gives no precipitate in the cold; neither does a dilute solution of a citrate with *chloride of calcium;* but on boiling the mixture (which must be neutral or alkaline), a white precipitate of basic citrate of calcium is formed, insoluble in alkalis, very slightly soluble in ammoniacal salts, soluble in free acids, and in chloride of copper. This precipitate is redissolved when the solution cools. With *acetate of lead*, citric acid gives a white precipitate, slightly soluble in ammonia. When heated with strong sulphuric acid, all citrates give off carbonic oxide; the mixture does not blacken or evolve sulphurous acid till heat has been applied for some time.

d. *Malic Acid*, $C^4H^4O^5H^2$ (bibasic).—Forms colourless crystals which deliquesce in the air: very soluble in water and alcohol; when heated, they are decomposed into maleic acid, $C^4H^4O^4$, which sublimes, and fumaric acid, isomeric with maleic, which remains behind ($C^4H^6O^5=C^4H^4O^4+OH^2$). By ignition it is carbonised, giving off a smell resembling that of tartaric acid. Most malates are soluble in water. A solution of malic acid or a malate is not precipitated by *chloride of calcium*, or *lime-water*, either in the cold or on heating; but on the addition of alcohol, a white precipitate of malate of calcium separates. Normal malate of calcium is also precipitated by long boiling of a solution of malic acid, nearly neutralised by milk of lime. This is the process by which malic acid is extracted from the juice of the berries of the mountain-ash. (c) With *acetate of lead*, malic acid gives a white precipitate, soluble in excess of malic acid or of ammonia: when this precipitate is heated with its mother liquid, it melts to a semi-fluid transparent mass. When any malate is heated with fuming sulphuric acid, the mixture is not blackened. This reaction distinguishes malic from citric and tartaric acids.

e. *Meconic Acid*, $C^7HO^7H^3$ (tribasic).—Exists in opium. The alkaline-earthy meconates are insoluble. With *sesquisalts of iron* meconic acid gives a deep red colour, closely resembling that produced by sulphocyanic acid; from which it is distinguished by its being destroyed by hydrochloric acid, and not affected by chloride of mercury (p. 42).

f. *Tannic Acid*, $C^{27}H^{22}O^{17}$.—(The basicity of tannic acid is not yet accurately determined; it is certainly polybasic.) Contained in gall-nuts. It forms an amorphous mass, which is generally coloured yellow by the action of the air. It is soluble in water, alcohol, and ether. Mineral acids precipitate it from its aqueous solution as a gelatinous mass insoluble in excess of acid. Its syrupy ethereal solution does not mix with excess of ether. With *sesquisalts of iron* tannic acid gives a bluish-black precipitate, which constitutes the colouring matter of ink; with *protosalts of iron* this precipitate only forms as the protosalt is gradually oxidised by exposure to the air. With *tartrate of antimony and potassium* (tartar emetic) it gives a white gelatinous precipitate. With solution of *gelatine* it gives a white precipitate, not absolutely insoluble in water, unless the tannic acid be in excess, in which case, the precipitate is greyish and aggregated to an elastic mass. It is owing to this property that tannic acid combines with animal skin, forming leather. Tannic acid is entirely removed from a solution by immersing in it a piece of skin: and the acid may be estimated by determining the increase in weight of the skin. With most organic alkaloids, tannic acid forms white compounds, insoluble in water, soluble in acetic acid.

g. *Gallic Acid*, $C^{7}H^{3}O^{5}H^{3}$ (tribasic).—By a gradual heat gallic acid is decomposed into pyrogallic acid, $C^{6}H^{6}O^{3}$, and carbonic anhydride. With *proto-* or *sesquisalts of iron*, it gives a bluish-black precipitate. It is distinguished from tannic acid by not precipitating a solution of *gelatine*. An alkaline solution of gallic acid absorbs oxygen from the air, becoming gradually yellow, green, red, and finally dark brown.

h. *Lactic Acid*, $C^{3}H^{6}O^{3}$ (bibasic?).—Formed by the fermentation of milk. It is a colourless liquid, readily soluble in water, alcohol, and ether. It is decomposed by heat, with evolution of carbonic oxide and formation of various compounds. All lactates are soluble in water, the alkaline lactates most readily: the *zinc-* and *calcium-*salts are easily crystallisable, and serve for the isolation and detection of lactic acid. For the detection of lactic acid in animal compounds (*e. g.* in the fluid extracted from flesh, in blood, urine, &c.), the liquid is evaporated to dryness and the residue treated with an alcoholic solution of oxalic acid, and filtered; the filtrate digested with oxide of lead, and again filtered; the filtrate, which contains all the lactic acid as lactate of lead, decomposed by hydrosulphuric acid, filtered off from the sulphide of lead, concentrated by evaporation, digested with oxide of zinc or excess of milk of lime, and the clear solution crystallised. Or the residue obtained by evaporation in the water-bath is treated with alcohol, the alcoholic solution evaporated to a syrup and mixed with its own volume of dilute sulphuric acid (1 vol. acid and 1 vol. water), and with three or four times its volume of alcohol. The alcoholic solution, which contains all the lactic acid, is mixed with ether until no fresh precipitate is produced by further addition of ether, filtered, the alcohol and ether distilled off, and the residue concentrated in the water-bath to a syrup: it is then mixed with half its volume of alcohol and five times its volume of ether, which dissolves out the lactic acid in a state of purity. After the removal of the ether by evaporation, the lactic acid is saturated with milk of lime, and the clear solution crystallised, and purified from sulphate of lime by recrystallisation from alcohol. The presence of lactic acid is most certainly ascertained by the ultimate analysis of the salt thus obtained. Lactic acid does not hinder the precipitation, by excess of lime-water, of oxide of copper from salts of copper. When heated with strong sulphuric acid, lactic acid gives off pure carbonic oxide, and the mixture is blackened. Heated with nitric acid it is converted into oxalic acid.

i. *Uric Acid*, $C^5H^2N^4O^3H^2$ (bibasic).—Contained in the excrement of serpents, in urinary calculi, human urine, guano, &c. It forms white, shining, crystalline scales, which are scarcely at all soluble in cold water, dilute hydrochloric or acetic acid; insoluble in alcohol and ether; soluble in alkalis and alkaline salts, from which solution acids precipitate uric acid. It is decomposed by heat, forming urea, cyanuric acid, carbonate and cyanide of ammonium, and hydrocyanic acid, and leaving a carbonaceous residue. (c) It is soluble in strong nitric acid, with evolution of gas: if this solution be evaporated nearly to dryness in the water-bath, and a drop of ammonia added, a magnificent purple-red colour is produced, owing to the formation of *murexide*, $C^8H^8N^6O^6$: the addition of caustic potash changes the colour to a bluish-purple. Very small traces of uric acid may be detected by this reaction. For the detection of uric acid in urine, a considerable quantity of urine is mixed with hydrochloric acid, and allowed to stand for one or two days, when the uric acid separates out. From urinary calculi it is obtained by boiling them with dilute potash, and saturating the filtrate with hydrochloric acid. From liquids containing albumen (as the serum of blood), hydrochloric acid precipitates albumen as well as uric acid. In this case the liquid is evaporated to dryness in the water-bath, the residue exhausted with alcohol, and treated with boiling water: the aqueous solution is concentrated by evaporation, and the uric acid precipitated from it by acetic acid, and tested by nitric acid and ammonia as above. When fused with caustic potash uric acid evolves ammonia: the residue, if not too strongly heated, contains cyanide and cyanate of potassium.

PART II.

REACTIONS OF THE METALLIC ELEMENTS AND THEIR SALTS.

The metallic elements, or metals, are capable of division into certain definite groups, the members of which exhibit similar reactions with a certain general reagent. There is, however, one metal, Hydrogen, which cannot be included in any of these groups, as it does not exhibit any characteristic reaction with any of the general reagents which serve for the classification of the metals. We shall therefore study this metal first, and then proceed to the consideration of the other metals in their several groups, taking first that group of metals which are most analogous to the non-metallic elements. By so doing we invert the order which is commonly adopted in works on analysis, according to which the alkaline metals are considered as the first group, while those which are most analogous to the non-metallic elements constitute the last group. The ordinary arrangement is attended with no conceivable advantage. Not only is it purely arbitrary, and is never followed in actual analysis, in which the metals analogous to the non-metallic elements are invariably separated first, and the alkaline metals last; but it also conceals the remarkable gradation of properties which exists between all elements, metallic and non-metallic, and which is indicated by the arrangement we have adopted.

Hydrogen. H. Atomic weight, 1.

A permanent colourless gas, devoid of smell: it is the lightest body known: it is inflammable, burning with an almost colourless flame, forming only water. It is but very slightly soluble in water. It combines with half its volume of oxygen, forming water; the combination takes place slowly on contact with platinum-black, which may be made into a ball with moist clay, and introduced into the gaseous mixture; or immediately, with explosion, on the application of a light. Equal volumes of hydrogen and chlorine combine with explosion when exposed to sunlight, forming hydrochloric acid; in the dark they combine very slowly or not at all. When hydrogen, or a gaseous mixture containing hydrogen, is passed over red-hot oxide of copper, or when an organic compound is heated to redness with excess of oxide of copper, *the whole* of the hydrogen is converted into water, which may be collected in a tube containing chloride of calcium, and the amount of hydrogen determined from the increase in weight of the tube. The carbon in organic compounds is converted by the same process into carbonic anhydride. This is the most general method for detecting the presence of hydrogen.

OXIDES OF HYDROGEN.—The most important oxide of hydrogen is *Water*, OH^2. It is a colourless liquid, devoid of taste or smell, and neutral to litmus-paper. When evaporated on platinum foil, it leaves no residue.

For the *detection* of water in solid non-volatile bodies, in minerals and salts, the substance under examination is heated to dull redness in a perfectly dry glass tube, closed at one end, which is held in a slanting position over the lamp; if any water be present it will be condensed in the cool part of the tube, either in the form of mist or of drops. In the case of organic compounds, the heat applied must not be sufficient to decompose them entirely.

The *estimation* of water, in substances which are not volatilised or decomposed by an elevation of temperature, is effected by simply heating them to a certain temperature, until they no longer lose weight, and determining the loss of weight sustained by them. The degree of heat necessary varies in different substances. Substances which cannot be dried by heat (*e. g.* gases, volatile liquids, &c.) are freed from water by contact with chloride of calcium, sulphuric acid, phosphoric anhydride, and other hygroscopic bodies. In substances which are decomposed by heat, the water is collected in a weighed chloride of calcium tube, and estimated directly by the increase in weight of the tube. This method is inapplicable when any of the products of decomposition (*e.g.* ammonia) are absorbed by chloride of calcium.

GROUP I.

Metals whose sulphides are insoluble in dilute mineral acids; which can, therefore, be completely precipitated by hydrosulphuric acid from a solution acidulated by nitric or hydrochloric acid.

This group contains two subdivisions:—

A. Metals whose sulphur compounds possess *acid* properties. These are *arsenic*, *antimony*, *tin*, *gold*, *platinum*, *iridium*, *selenium*, *tellurium*, *molybdenum*, *wolfram*, *vanadium*. Their sulphides are soluble in alkaline sulphides, and form therewith sulpho-salts, which are generally analogous to the oxygen salts of the same elements, oxygen being replaced by sulphur.

B. Metals whose sulphur compounds do *not* possess acid properties. These are *lead*, *silver*, *mercury*, *bismuth*, *copper*, *cadmium*, *palladium*, *rhodium*, *osmium*, *ruthenium*. Their sulphides are insoluble in alkaline sulphides. (Sulphide of mercury is soluble in sulphide of potassium, or sodium; sulphide of copper is somewhat soluble in sulphide of ammonium.)

The metals of these two subdivisions are very readily separated. Their acid solution is completely precipitated by hydrosulphuric acid (the precipitation being facilitated by gentle heat), and the precipitate digested with an excess of sulphide of ammonium, or sulphide of potassium; when the sulphides of the metals of the second division remain undissolved, while those of the first division are completely dissolved. The addition of dilute hydrochloric acid, reprecipitates the dissolved sulphides, with evolution of hydrosulphuric acid ($2SbS^4K^3 + 6ClH = Sb^2S^5 + 3SH^2 + 6ClK$); and, if the alkaline sulphide employed contained any sulphur compound higher than the protosulphide, with separation of sulphur.

Group I.—Subdivision A.

1. **Arsenic.** As. Atomic weight, 75.

Arsenic is found native as sulphide of arsenic; as metallic arsenides (chiefly in combination with iron, nickel, and cobalt); and as arsenates (of calcium, magnesium, lead, &c.). Traces of it are almost invariably found in sulphur, iron, copper, tin, and antimony; and it also exists in the deposit from several mineral springs. It is a brittle metal, easily powdered; in contact with moist air it loses its metallic lustre, is oxidised and covered with a brown coating, from which arsenious acid may be dissolved by water or hydrochloric acid. It is completely volatile; when heated in contact with air, it burns and forms arsenious anhydride, giving off at the same time a penetrating smell of garlic. It is not attacked by hydrochloric acid; nitric acid oxidises it into arsenious acid, or, if very concentrated, partly into arsenic acid. Chlorine combines violently with metallic arsenic at the ordinary temperature, forming liquid terchloride of arsenic. Chlorine, aqua-regia, or hydrochloric acid and chlorate of potassium oxidise all arsenic compounds, without exception, to arsenic acid: the same effect is produced by the fusion of an arsenic compound with a nitrate.

OXIDES OF ARSENIC. *Arsenious Anhydride*, As^2O^3. *Arsenic Anhydride*, As^2O^5.

a. *Arsenious Anhydride. Arsenious Oxide.* As^2O^3.—Obtained either as a white powder, or as a transparent glassy mass, which becomes opaque by exposure to the air, without, however, absorbing any moisture. It can be obtained in definite octahedral crystals, either by sublimation, or by crystallisation from a hot saturated aqueous solution. It is completely volatile; its vapour is free from smell; the characteristic garlic smell of arsenic is only perceived when arsenious oxide is heated in contact with charcoal, or some other reducing agent. It is a violent poison. It is difficultly soluble (in about 50 parts) in cold water; more easily (in 10 to 12 parts) in hot water; still more easily in hydrochloric acid, or alkalis. The aqueous solution contains *arsenious acid*, $AsHO^3H^2$, analogous to phosphorous acid: the alkaline solution contains an alkaline arsenite.

Arsenious acid forms a definite series of salts, which are closely analogous to the phosphites: many of them are insoluble in water. An aqueous solution of an arsenite is coloured yellow by *hydrosulphuric acid*, but is not precipitated unless free acid be present, in which case the whole of the arsenic is precipitated as tersulphide (As^2S^3), of a lemon-yellow colour. Tersulphide of arsenic is readily soluble in caustic alkalis (whether fixed or volatile) forming an alkaline arsenite and sulpharsenite, ($As^2S^3 + 4KHO = AsS^3HK^2 + AsO^3HK^2 + OH^2$), in alkaline carbonates, sulphites, and sulphides, and in nitric acid: it is insoluble in hydrochloric acid. From any of these solutions it is completely reprecipitated as tersulphide on neutralisation with nitric or hydrochloric acid, (For other reactions of As^2S^3, see p. 86.) With *nitrate of silver*, after exact neutralisation with ammonia, arsenious acid gives a yellow precipitate: with *sulphate of copper*, after neutralisation, a yellowish-green precipitate (Scheele's green): with excess of *lime-water*, a white precipitate. The two first of these precipitates are readily soluble in ammonia, chloride of ammonium, and nitric acid; the last in nitric acid and ammoniacal salts. Arsenious acid is not precipitated by a mixture of ammonia, chloride of ammonium, and a magnesium-salt. Arsenious acid is a powerful reducing agent, being itself oxidised into arsenic acid. Thus, with *terchloride of gold*, its acid solution gives a precipitate of metallic gold, from the weight of which the amount of arsenious acid may be calculated, 3 atoms arsenious acid reducing 2 atoms of gold ($3AsO^3H^3 + 2Cl^3Au + 3OH^2 = 3AsO^4H^3 + Au^2 + 6ClH$): with *bichromate* and *permanganate of potassium* it gives a green and brown-yellow colour respectively. When a solution of an alkaline arsenite is heated with *a little sulphate of copper*, a red precipitate of suboxide of copper is formed ($AsHO^3K^2 + 2SO^4Cu^2 + 2OH^2 = AsO^4H^3 + SO^4K^2 + SO^4H^2 + Cu^4O$). A solution of arsenious acid in excess of carbonate of sodium takes up iodine, forming arsenic acid and a metallic iodide ($AsHO^3Na^2 + Na^2O + I^2 = AsO^4Na^2H + 2INa$). If a little starch paste be added to the mixture, the first appearance of a blue tint marks exactly the point at which all the arsenious acid is converted into arsenic acid. (On this reaction is founded a method for the volumetric estimation of chlorine, iodine, &c., p. 249.) If clean metallic *copper* be immersed in a hydrochloric acid solution of arsenious acid, a grey precipitate of metallic arsenic is formed on the copper. (Reinsch's test.) When arsenious (or arsenic) acid is brought into contact with metallic *zinc* and dilute hydrochloric or sulphuric acid in a Marsh's apparatus, hydrogen is evolved together with arsenide of hydrogen, AsH^3, a gas which has a very nauseous smell and is inflammable, burning with a bluish-white flame, and forming water and arsenious anhydride. If a cold surface, *e. g.* a fragment of porcelain, be introduced into the flame, shining stains of metallic arsenic are deposited upon it, which, according to the quantity of arsenic present, are of a brown, steel-grey, or almost black colour. Very small traces of arsenic may be detected in this manner. The arsenic spots disappear on the addition of a drop of a strong alkaline solution of hypochlorite of sodium; or they are dissolved by a drop of hot nitric acid, forming a clear solution which contains either arsenious or arsenic acid. If a drop of nitrate of silver be now added to this solution, and a glass-rod moistened with ammonia be held over it (without touching it), a yellow or red precipitate of arsenite or arsenate of silver is formed. If the arsenic spots be exposed to an atmosphere of moist chlorine (evolved in the cold from chloride of lime and a dilute acid), they at once disappear; and if a drop of nitrate of silver be then dropped on the place where the arsenic spot was, a reddish precipitate is formed, consisting of arsenate and chloride of silver. If the arsenide of hydrogen (previously dried by passing through a chloride of calcium tube) be led through a narrow tube of hard glass, free from lead, which is drawn out to a point at the further end, and the middle of the tube heated to redness over the lamp, a dark-brown shining ring of metallic arsenic is deposited in the tube, beyond the heated portion; if arsenic be present in any quantity, the ring is completely opaque. The arsenic deposit is readily volatile, and may be driven hither and thither in the tube by the application of heat, while a stream of hydrogen is kept passing through the tube: the arsenic does not fuse into globules, and the gas that issues from the tube has a distinct smell of garlic. If the arsenic deposit be heated while a stream of hydrosulphuric acid is passed through the tube, it is entirely converted into volatile yellow tersulphide of arsenic, which is not decomposed by hydrochloric acid. If arsenide of hydrogen be led into hot concentrated nitric acid, a clear solution of arsenic acid is formed; if it be led into a solution of nitrate of silver, arsenite of silver is formed, which is retained in solution by the free nitric acid, and is precipitated yellow on the neutralisation of the free acid by ammonia. This property of forming a gaseous compound with hydrogen, from which a metallic deposit may be obtained, distinguishes arsenic from every other metal except antimony, which, under the same circumstances, yields a metallic deposit very closely resembling in appearance that of arsenic: it may, however, be distinguished from the arsenic deposit by several reactions, which will be enumerated under the head of Antimony (p. 90).

The vapour of arsenious anhydride is easily reduced by passing over redhot charcoal, metallic arsenic being separated ($As^2O^3 + C^3 = As^2 + 3CO$). Thus, if a fragment of arsenious anhydride be placed in the closed end of a very narrow tube, and two or three splinters of freshly ignited charcoal, about half an inch long, be placed above it, and, the tube being held horizontally, the part of it containing the charcoal heated to redness before the arsenious anhydride is volatilised, a dark shining ring of metallic arsenic will be formed in the tube beyond the charcoal: this ring may be driven by heat from one part of the tube to another, till it is entirely oxidised by the air in the tube, and converted into colourless, shining, volatile crystals of arsenious anhydride, the octahedral form of which may be clearly discerned through a magnifying glass. When arsenious anhydride is fused with cyanide of potassium, cyanate of potassium is formed, and the whole of the arsenic volatilised ($As^2O^3 + 3CyK = 3CyOK + As^2$). When a fragment of arsenious anhydride about the size of a pin's head is heated in a test-tube with about the same quantity of dry acetate of potassium, oxide of kakodyl is formed, and easily recognised by its peculiarly offensive smell ($4C^2H^3O^2K + As^2O^3 = C^4H^{12}As^2O + 2CO^3K^2 + 2CO^2$). When arsenious acid or any other arsenic compound is mixed with a large excess of organic matter, it may be separated therefrom by distillation with chloride of sodium and excess of concentrated sulphuric acid, when terchloride of arsenic passes over into the distillate, where it gives the ordinary reactions of arsenious acid. The whole of the arsenic cannot be separated in this manner.

b. *Arsenic Anhydride. Arsenic Oxide.* As^2O^5.—A white opaque mass, which, when freshly fused, has a glassy appearance. By ignition it is decomposed into arsenious anhydride and oxygen, and volatilises entirely, leaving no residue. It absorbs moisture from the air and gradually liquefies: and is then readily soluble in 6 parts cold and 2 parts hot water. The solution, which has a strong acid reaction, contains *Arsenic Acid*, AsO^4H^3, a tribasic acid, precisely analogous to phosphoric acid. Most arsenates are colourless, and isomorphous with the corresponding phosphates: those which are not soluble in water are soluble in nitric or hydrochloric acid.

A solution of an arsenate acidified by hydrochloric acid is very slowly precipitated by *hydrosulphuric acid* at the ordinary temperature, not less than twenty-four hours being necessary for complete precipitation: the precipitation is facilitated by gently heating the solution while the gas is being passed into it. The precipitate is pentasulphide of arsenic, As^2S^5: it resembles As^2S^3 in colour and in behaviour to solvents; but its solution in an alkali contains an alkaline arsenate as well as a sulpharsenate, ($As^2S^5 + 4OKH = AsS^4K^2H + AsO^4K^2H + SH^2$). If the acidified solution of an arsenate be heated with sulphurous acid, until the smell of the latter has entirely disappeared, the arsenic acid is reduced to arsenious acid ($AsO^4H^3 + SO^3H^2 = AsHO^3H^2 + SO^4H^2$), which is precipitated by hydrosulphuric acid much more speedily than arsenic acid. In order to effect a complete reduction, the treatment with sulphurous acid must be continued for some hours. When As^2S^5 is dissolved in ammonia, nitrate of silver added, and the whole exactly neutralised with nitric acid, a reddish-brown precipitate is formed: As^2S^3, when similarly treated, gives a yellow precipitate. With *nitrate of silver* a neutral arsenate gives a reddish-brown precipitate of AsO^4Ag^3: with *sulphate of copper*, a pale greenish-blue precipitate of AsO^4Cu^2H: with *lime-water* a white precipitate: all soluble in nitric acid and ammoniacal salts. With *sesquisalts of iron* and *uranium* it gives a yellowish-white precipitate, with *lead*-salts a white precipitate, whose behaviour to reagents resembles that of the corresponding phosphates. Arsenate of lead, however, when heated on charcoal before the blowpipe, does not crystallise on cooling: in the inner flame it is reduced to metallic lead, while the smell of arsenic vapours is distinctly perceived. With *molybdate of ammonium*, and *sulphate of magnesium, ammonia, and chloride of ammonium*, the reactions of arsenic acid precisely resemble those of phosphoric acid (pp. 58, 60). Arsenic acid is always estimated as arsenate of magnesium and ammonium, $AsO^4Mg^2NH^4$: in this case the precipitate must be dried in the water-bath and weighed as $AsO^4 \cdot Mg^2NH^4 + \frac{1}{2}H^2O$; for if it be ignited, as directed for the corresponding phosphate, a loss would ensue from the volatilisation of a portion of the arsenic. When a solution of an arsenate or arsenite acidified with hydrochloric acid is heated to boiling with hyposulphite of sodium, tersulphide of arsenic is precipitated ($2AsO^3H^3 + 3S^2O^3Na^2 = As^2S^3 + 3SO^4Na^2 + 3OH^2$).—Vohl. (Ann. Ch. Pharm. xcvi. 238.) In Marsh's apparatus, arsenates, like arsenites, evolve arsenide of hydrogen.

Distinction and separation of arsenic and arsenious acids.—Arsenic acid is completely precipitated by a mixture of ammonia, chloride of ammonium, and a soluble magnesium-salt, while arsenious acid is not precipitated at all by this reagent: hence all the arsenic acid may be removed from a solution as arsenate of magnesium and ammonium, and the filtrate acidified with hydrochloric acid, and saturated with hydrosulphuric acid, when, if arsenious acid be present, yellow As^2S^3 is precipitated. Arsenious acid reduces terchloride of gold: arsenic acid does not. In those arsenates which are only soluble in acids (which therefore, cannot be precipitated by a magnesium-salt), the arsenic acid is detected by neutralising the solution as nearly as possible with ammonia, and adding acetate of sodium and a *very little* sesquichloride of iron, when sesquiarsenate of iron is precipitated.

Arsenic acid is distinguished from phosphoric acid by its precipitation from an acid solution by hydrosulphuric acid. The arsenate of magnesium and ammonium, and the sesquiarsenate of iron are distinguished from the corresponding phosphates by their evolving arsenide of hydrogen in Marsh's apparatus, and by their behaviour before the blow-pipe (p. 87).

Sulphides of Arsenic.—The two principal sulphides of arsenic correspond to its two oxides; tersulphide, As^2S^3, corresponding to As^2O^3, and pentasulphide, As^2S^5, to As^2O^5. These sulphides, like the oxides, are capable of forming acids perfectly analogous to the oxygen acids, the oxygen being replaced by sulphur: thus, As^2S^3 forms *sulpharsenious acid*, $AsHS^3H^2$, analogous to arsenious acid, $AsHO^3H^2$; and As^2S^5 forms *sulpharsenic acid*, AsS^4H^3, analogous to arsenic acid, AsO^4H^3. Alkaline salts of these acids are formed when the sulphides are dissolved in alkaline sulphides. These sulpho-salts are decomposed by mineral acids, the arsenic being reprecipitated as sulphide, and hydrosulphuric acid being evolved—($2AsS^4K^3+6ClH=As^2S^5+6ClK+3SH^2$; and $2AsHS^3K^2+4ClH=As^2S^3+4ClK+3SH^2$).

When either sulphide of arsenic is fused, even in the smallest quantity, in a glass tube with cyanide of potassium, a ring of metallic arsenic is formed in the tube. Sulphocyanate of potassium is thus formed, together with a sulpharsenic salt, which latter is not decomposed by cyanide of potassium: hence all the arsenic present cannot be reduced and volatilised in this manner. If the sulphide of arsenic be mixed with excess of sulphur, the whole of the arsenic goes to form a sulpharsenic salt, and no metallic deposit is obtained. The presence of certain easily reducible metals (copper, lead, iron, nickel, cobalt, silver, gold—but not bismuth or antimony) hinders the formation of a metallic deposit on fusion with cyanide of potassium. When As^2S^3 is fused with an alkaline carbonate in a glass tube, a ring of metallic arsenic is obtained, and the fused mass contains a mixture of an alkaline arsenate and sulpharsenate ($5As^2S^3=3As^2S^5+As^4$, and $3As^2S^5+12OKH=3AsS^4K^2H+3AsO^4K^2H+3SH^2$.) If this mixture of arsenate and sulpharsenate be heated in a stream of hydrogen, or in contact with charcoal, the arsenic contained in the arsenate is reduced to the metallic state, but not that contained in the sulpharsenate. Hence no metallic deposit is obtained by fusing As^2S^5, or As^2S^3 mixed with sulphur, with an alkaline carbonate. In this manner As^2S^3 may be distinguished from As^2S^5.

In order to employ the above reactions of the tersulphide of arsenic with an alkaline cyanide or carbonate for the detection of very small traces of arsenic (as in judicial investigations), the following is the best method of proceeding:—1 part of As^2S^3 (which must not contain any free sulphur) is dried and mixed with 12 parts of a perfectly dry powder, consisting of 1 part cyanide of potassium and 3 parts carbonate of sodium, and the mixture introduced by means of a slip of stiff paper into a tube of hard glass 9 or 10 inches long, which is drawn out at one end to a thin open point about an inch in length. The tube is then connected by the end not drawn out with an apparatus in which carbonic anhydride is generated by the action of hydrochloric acid on marble, and a slow stream of carbonic anhydride, previously dried by passing through strong sulphuric acid, led through the tube. The mixture in the tube is first gently heated, in order to expel all moisture from it; the tube is then heated to redness, between the mixture and the pointed end, and finally the mixture itself is strongly ignited; when a ring of metallic arsenic will be deposited at the commencement of the point. It is of importance that all moisture should be expelled from the mixture before it is ignited, and that the stream of carbonic anhydride should be very slow. Sulphide of antimony gives no metallic deposit under these circumstances.—Fresenius and Babo.

Blowpipe reactions.—When any arsenic compound is heated on charcoal (either alone or with carbonate of sodium and cyanide of potassium) in the inner blowpipe flame, the characteristic garlic smell is at once perceived, by which the smallest trace of arsenic may be detected.

Arsenic may be completely separated from all metals whose sulphides are not volatile, by heating the mixed sulphides or oxides in a stream of hydrosulphuric acid.

The detection of arsenic is one of the easiest, and at the same time one of the most important problems, in analytical chemistry. The volatility of all its compounds, its exceedingly easy reduction to the metallic state, coupled with its characteristic smell, its complete precipitation by hydrosulphuric acid from an acid solution, the formation of arsenide of hydrogen when any arsenic compound is brought in contact with zinc and sulphuric acid. form an *ensemble* of reactions which in completeness and precision, are equalled by those of few other metals.

Estimation of Arsenic.—Arsenic is best estimated as arsenate of magnesium and ammonium (see p. 85).

2. **Antimony.** Sb. Atomic weight, 120.

Found in nature generally as sulphide, in combination with other metallic sulphides, as the protosulphides of lead and iron, tersulphide of arsenic, and subsulphide of copper. It is a very lustrous metal, of a bluish-white colour; very brittle and easily powdered. At the ordinary temperature it is not affected by the air: when strongly heated it volatilises entirely, forming white fumes of antimonous oxide, which are destitute of smell. It is scarcely attacked at all by hydrochloric acid, even on boiling: aqua-regia dissolves it readily, forming terchloride of antimony: nitric acid converts it into a mixture of antimonous and antimonic anhydrides, insoluble in nitric acid, soluble in tartaric acid. By fusion of an antimony compound with nitrate of potassium, the antimony is entirely oxidised to antimonic acid. Chlorine attacks antimony violently at the ordinary temperature, with great evolution of heat, forming volatile ter- or penta-chloride of antimony, Cl^3Sb or Cl^5Sb, according to the proportions of antimony and chlorine employed. All sulphur compounds of antimony are soluble in hot concentrated hydrochloric acid, with evolution of hydrosulphuric acid, and (in the case of compounds containing more sulphur than Sb^2S^3) with separation of sulphur.

OXIDES OF ANTIMONY. *Antimonic Oxide,* Sb^2O^3; *Antimonic Anhydride,* Sb^2O^5; *Intermediate Oxide,* Sb^4O^8.—Antimony is less closely analogous to phosphorus and the non-metallic elements than arsenic is. Its highest oxide combines with water and forms an acid, *antimonic acid;* but the acid properties of the lower oxide are less clearly defined; for, though under certain circumstances it appears to be capable of forming *antimonites,* it is generally met with in salts in which antimony plays the part of a base.

a. *Antimonic Oxide. Antimonous Anhydride.* Sb^2O^3.—A white powder, which when heated fuses to a yellow mass, and at a red heat sublimes entirely, forming crystalline needles. It is very sparingly soluble in water: soluble in tartaric acid: nitric acid oxidises it into insoluble antimonic anhydride, or into the intermediate oxide, Sb^1O^8: hydrochloric acid dissolves it readily, forming terchloride, Cl^3Sb. The best solution in which to study the reactions of antimony-salts in the wet way is one of Cl^3Sb, in which the precipitate produced by dilution is redissolved in hydrochloric acid. Antimony-salts are very unstable: they are decomposed by *water*, with precipitation of a white insoluble basic salt. Tartaric acid prevents this decomposition. *Hydrosulphuric acid* precipitates the whole of the antimony as tersulphide, Sb^2S^3, of an orange-red colour, soluble in alkaline sulphides and in caustic potash, slightly soluble in ammonia, insoluble in acid carbonate or sulphite of ammonium. A neutral dilute solution of tartar-emetic (tartrate of antimony and potassium) is only coloured orange by hydrosulphuric acid: on addition of hydrochloric acid, Sb^2S^3 is precipitated. *Caustic potash* precipitates Sb^2O^3, soluble in excess: *ammonia* and *alkaline carbonates* precipitate Sb^2O^3, insoluble, or very slightly soluble, in excess: *oxalic acid* gradually precipitates all the antimony as Sb^2O^3. Tartaric acid prevents the precipitation in all these cases. *Chromic acid* oxidises an acid solution of Sb^2O^3 into antimonic acid. *Terchloride of gold* is reduced by $SbCl^3$: antimonic acid generally separates out together with the metallic gold. By this reaction Sb^2O^3 may be estimated in presence of antimonic acid. With a solution of antimonic oxide in potash, *terchloride of gold* and *nitrate of silver* give black precipitates, the latter of which is insoluble in ammonia. These are the most delicate reactions for the detection of Sb^2O^3, and distinguish it perfectly from antimonic acid. Metallic *zinc*, *iron*, and *tin*, immersed in terchloride of antimony, give a black precipitate of metallic antimony. With zinc and dilute sulphuric acid (in Marsh's apparatus), terchloride of antimony, or any antimony compound except the sulphides, evolve gaseous antimonide of hydrogen, SbH^3, an inflammable gas, very closely resembling AsH^3. Like AsH^3 it is decomposed by passing through a glass tube heated to redness in one spot, and a ring of metallic antimony is deposited in the cool part of the tube. This is less volatile than the arsenic deposit: when heated it fuses into small shining globules before volatilising, which are visible through a magnifying glass, and no garlic smell is produced. If the antimony deposit be heated in a stream of hydrosulphuric acid, it is converted into sulphide of antimony, of a black, or partly orange, colour; which, when heated in a stream of hydrochloric acid gas, completely disappears, being decomposed into hydrosulphuric acid and volatile terchloride of antimony. If SbH^3 be kindled, and a fragment of porcelain introduced into the flame, metallic stains are deposited, which are blacker and less shining than those of arsenic, and are insoluble in hypochlorite of sodium. Nitric acid does not dissolve them, but converts them into an insoluble mixture of antimonic oxide and anhydride. If the excess of acid be gently evaporated the residue gives a black precipitate with ammonio-nitrate of silver. When exposed to moist chlorine, they disappear, like the arsenic stains: but a drop of nitrate of silver dropped on the place where they were gives only a white precipitate. A drop of nitric and of hydrochloric acid dissolves them completely, and when the excess of acid is carefully driven off by evaporation, the solution gives an orange precipitate with hydrosulphuric acid. When moistened with sulphide of ammonium and evaporated, they become orange. When led into hot concentrated nitric acid, SbH^3 gives a white precipitate of antimonic acid, which, after evaporation of the free acid, and treatment with hot water, remains insoluble. When led into nitrate of silver, all the antimony is precipitated as black antimonide of silver, $SbAg^3$.

b. *Antimonic Anhydride*, Sb^2O^5.—A yellow powder, which on ignition loses oxygen and becomes white, being converted into antimonous-antimonic oxide, Sb^4O^8. In combination with water it forms *antimonic acid*, a white powder, insoluble in water. Antimonic acid seems to exist under two modifications, which very closely resemble each other, and so are distinguished with much difficulty. The first, of which the potassium-salt is obtained by heating antimony with nitrate of potassium, is insoluble in water and in ammonia, soluble, though not readily, in hydrochloric and tartaric acids, and partially precipitated from the hydrochloric acid solution by water. The second, (*metantimonic acid*) is obtained by the precipitation of pentachloride of antimony by water, or by the fusion of an alkaline antimonate with excess of caustic alkali: it is gradually soluble in ammonia, and in a large excess of cold water, and is precipitated from these solutions by acids. Metantimonate of potassium serves as a reagent for the detection of sodium, metantimonate of sodium being difficultly soluble in water, and insoluble in alcohol. In an aqueous solution it is gradually converted into ordinary antimonate of potassium, which does not precipitate sodium-salts, and is precipitated by chloride of ammonium.

A hydrochloric acid solution of antimonic acid is precipitated as orange pentasulphide, Sb^2S^5, by *hydrosulphuric acid:* this precipitate forms somewhat more slowly than Sb^2S^3. With *terchloride of gold* and *oxalic acid* it gives no precipitate: when heated with *chloride of tin* it is reduced, and antimonic oxide precipitated: *protosalts of iron* do not reduce it. A solution of antimonate of potassium gives with *nitrate of silver* a yellowish-white precipitate of antimonate of silver, readily soluble in ammonia. With *terchloride of gold* it gives no precipitate.

c. By the ignition of antimonic acid or anhydride, an oxide, Sb^4O^8, is formed, intermediate between Sb^2O^3 and Sb^2O^5. It may be regarded as a compound of 1 atom antimonic oxide, with 1 atom antimonic anhydride ($Sb^4O^8 = Sb^2O^3 + Sb^2O^5$); or as antimonate of antimony (SbO^4Sb). It is the best form in which to determine antimony: for the product obtained by the oxidation of the sulphides of antimony, itself not constant in composition, is entirely converted by ignition into Sb^4O^8.

Distinction of the Oxides of Antimony from each other.—Bunsen (Ann. Ch. Pharm. cvi. 1.) states that Sb^2O^3 may be distinguished from Sb^4O^8 and Sb^2O^5 by means of hydriodic acid. When either Sb^4O^8 or Sb^2O^5 are heated with pure iodide of potassium and hydrochloric acid, iodine is set free, and a dark coloured solution formed; when Sb^2O^3 is similarly treated, a yellow solution is formed, no iodine being liberated. The teriodide being the highest iodine compound of antimony, in the case of the two higher oxides there must be more iodine liberated than is capable of combining with the antimony ($Sb^2O^5 + 10IH = 2I^3Sb + I^4 + 5OH^2$), while with Sb^2O^3 the amount of iodine liberated is exactly what is requisite to combine with the antimony ($Sb^2O^3+6HI=2I^3Sb+3OH^2$). Sb^2O^5 is distinguished from Sb^4O^8 and Sb^2O^3 by the fact that the two lower oxides reduce ammoniacal nitrate of silver, giving a brown or black precipitate, while Sb^2O^5 has no reducing action.

SULPHIDES OF ANTIMONY.—The two most important sulphides of antimony are Sb^2S^3 and Sb^2S^5, corresponding to Sb^2O^3 and Sb^2O^5 respectively. They are both orange-yellow, insoluble in dilute hydrochloric acid, soluble in nitric or strong boiling hydrochloric acid. They are both soluble in alkaline sulphides, forming sulphantimonites and sulphantimonates, sulpho-salts entirely analogous to those of arsenic: the solution is decomposed by hydrochloric acid, and the sulphide reprecipitated.

Blowpipe reactions.—All antimony compounds, (except the sulpho-salts) when heated on charcoal before the blowpipe with cyanide of potassium or carbonate of sodium, give a *brittle* globule of metallic antimony, which may be volatilised entirely by continued heat, and, if it contain no arsenic, evolves no smell of garlic: at the same time the charcoal is covered with a white deposit of Sb^2O^3, which, when heated, volatilises readily. The compounds of the oxides or sulphides of antimony with a fixed alkaline base are entirely decomposed and volatilised by repeated ignition with chloride of ammonium, a fixed alkaline chloride being left behind.

Separation of Antimony from Arsenic.—The presence of arsenic in metallic antimony is easily detected by the garlic smell that is evolved when the metal is heated before the blowpipe. Sulphide of antimony must be reduced to the metallic state by fusion with carbonate of sodium and cyanide of potassium: in examining commercial sulphide of antimony, it is best to operate only on the residue which is left after treating a considerable quantity of the finely powdered sulphide with strong hydrochloric acid. From a freshly precipitated mixture of the sulphides of the two metals, all the sulphide of arsenic may be removed by digestion with carbonate of ammonium, while the sulphide of antimony remains undissolved. The two metals may also be detected in presence of each other by the different reactions (given above) of the metallic deposits obtained by means of Marsh's apparatus. The first spots deposited by a solution containing both metals consist of pure arsenic. The presence of a small amount of antimony does not prevent the complete solution of an arsenic spot in hypochlorite of sodium.

For the complete quantitative separation of arsenic and antimony, the following is the best method. The two metals, their sulphides, or their oxides, are completely dissolved in aqua-regia, or in hydrochloric acid and chlorate of potassium : to the solution is added tartaric acid, chloride of ammonium, and excess of ammonia. If any precipitate be produced, it must be dissolved in more tartaric acid or chloride of ammonium. The arsenic acid is then completely precipitated by sulphate of magnesium, as $AsO^4Mg^2NH^4$, thoroughly washed with dilute ammonia, dried in a water-bath, and weighed. The antimony is then precipitated from the acid solution by hydrosulphuric acid.

Bunsen (Ann. Ch. Pharm. cvi.) states that the sulphide of arsenic may be separated from that of antimony by acid sulphite of potassium, which dissolves the sulphide of arsenic, but not that of antimony. He proceeds as follows. To the solution of the sulphides in sulphide of potassium, a large excess of aqueous sulphurous acid is added, and the whole evaporated in the water-bath, till $\frac{2}{3}$ of the water, and all the free sulphurous acid are expelled : when the sulphide of antimony remains undissolved, while all the arsenic is contained in the solution as arsenious acid, and may be precipitated by hydrosulphuric acid. If sulphide of tin be present, it will be left undissolved together with the sulphide of antimony.

Another method, founded on the insolubility of metantimonate of sodium, will be described under the head of Tin (p. 98).

Antimony is frequently found in minerals in the form of sulphide, combined with one or more basic metallic sulphides. The methods employed for the separation of the antimony, vary in different cases. In zinkenite (sulphide of antimony and copper) and bournonite (sulphide of antimony, copper, and lead) the finely powdered mineral is oxidised by nitric acid, the solution saturated with potash, and digested with yellow sulphide of potassium: or the mineral is fused with three parts dry carbonate of sodium and two parts sulphur, in a covered porcelain crucible, and the fused mass, when cool, digested in hot water: when, in either case, the sulphide of antimony is dissolved, while the sulphides of copper and lead remain behind. Red silver-ore ($3Ag^2S, Sb^2S^3$) is decomposed by heating in a current of chlorine, when the antimony and sulphur are volatilised as chlorides, while chloride of silver remains behind. Commercial sulphide of antimony, when finely powdered, is soluble in fuming hydrochloric acid, or more easily in aqua-regia.

Bunsen (loc. cit.) recommends that antimony be always estimated as Sb^4O^8. Fuming nitric acid may be employed for the oxidation of the sulphide; but he prefers fusing the sulphide, freed from excess of sulphur by washing with bisulphide of carbon, with oxide of mercury, a large excess of which must be used, in order to avoid the risk of explosion. By ignition the excess of oxide of mercury is expelled, and the antimony left in the form of Sb^4O^8.

3. **Tin.** Sn. Atomic weight, 118.

Generally found in nature in the form of binoxide, as tin-stone. Tin is a white, malleable, easily fusible metal: it is not affected by exposure to the air at the ordinary temperature; but, when heated in the air, it becomes covered with a film of stannic oxide. It is soluble in hot hydrochloric acid, with evolution of hydrogen, and formation of chloride of tin, Cl^2Sn: in aqua-regia, with formation of perchloride of tin, Cl^4Sn: nitric acid converts it into stannic oxide, insoluble in the acid: heated in contact with chlorine it forms volatile Cl^4Sn.

OXIDES OF TIN. *Stannous Oxide*, or *Protoxide of Tin*, SnO. *Stannic Oxide*, or *Binoxide of Tin*, SnO^2.—Stannous oxide has no acid properties: in all stannous salts the tin is basic. Stannic oxide exhibits acid properties, forming two definite hydrates, which are weak acids.

a. *Stannous Oxide. Protoxide of Tin.* SnO.—A blackish-brown powder, which, when heated in contact with the air, takes fire, and is converted into binoxide. Stannous hydrate is white:

it dissolves in acids, forming *protosalts of tin*, or *stannous salts.* These salts are colourless: those which are neutral are partially precipitated by water: they absorb oxygen from the air, forming white binoxide, which is precipitated if there be not enough free acid present to hold it in solution. The best solution in which to study the reactions of protosalts of tin, is the chloride, Cl^2Sn. *Hydrosulphuric acid*, or *sulphide of ammonium* gives a dark-brown precipitate of sulphide of tin, SnS, which, by digestion with an alkaline sulphide, is converted into bisulphide, SnS^2, and so dissolved: the addition of hydrochloric acid to the solution precipitates yellow bisulphide. *Ammonia* and *alkaline carbonates* give a white precipitate of hydrate, insoluble in excess: the hydrate is soluble in excess of *potash*, and a brownish precipitate separates on boiling the solution. Chloride of tin is a very powerful reducing agent: it absorbs oxygen from the air and from water: it reduces sesquisalts of iron to protosalts, salts of copper to subsalts, chromic acid to chromic oxide. It reduces the metal from the salts of many of the heavy metals: (c) with *terchloride of gold*, an acid solution of chloride of tin gives a purple precipitate (in very dilute solutions a purple tinge only) insoluble in hydrochloric acid: with *chloride of mercury*, it gives a white precipitate of subchloride, which, if chloride of tin be in excess, and heat applied, is further reduced to grey metallic mercury. When heated with sulphurous acid, yellow bisulphide and white binoxide of tin are formed ($6Cl^2Sn + 2SO^3H^2 + 4OH^2 = 5SnO^2 + SnS^2 + 12ClH$).

b. *Stannic Oxide* or *Anhydride. Binoxide of Tin.* SnO^2.— A white powder, which, after ignition, has a yellowish tinge: it is then insoluble in water and acids, especially in nitric acid. By ignition with excess of chloride of ammonium, it may be volatilised completely. Like antimonic anhydride, it appears to exist in two modifications, each of which forms a definite hydrate, which differ very considerably in several of their reactions. Each of these hydrates is an acid; and, since one of them saturates a larger proportion of base than the other, we may call that which has the highest capacity of saturation *stannic*, the other, *metastannic*, acid. *Stannic acid* is obtained as a white precipitate when perchloride of tin, Cl^4Sn, is treated with ammonia, or largely diluted with water and heated. It is soluble in hydrochloric acid, the solution is not precipitated by acids, and the presence of tartaric acid prevents its precipitation by ammonia. *Carbonate of potassium* gives an abundant white precipitate, soluble in excess of the reagent: *gallic acid* gives no precipitate. *Metastannic acid* is the insoluble white compound produced by the action of strong nitric acid on metallic tin: it can only be dissolved in hydrochloric acid by long boiling and addition of water. Its solution is entirely precipitated by *sulphuric acid*, or by *ammonia*, even in presence of tartaric acid. *Carbonate of potassium* gives a white precipitate, insoluble in excess; *gallic acid*, after some time, gives a yellowish-white precipitate. Both stannic and metastannic acids are precipitated from their hydrochloric acid solutions on boiling, especially in presence of alkaline sulphates: the precipitation is the more speedy the less free acid is present. Both are completely soluble in caustic potash or soda. Both are precipitated from their acid solution by *hydrosulphuric acid* (especially when gently heated) as yellow bisulphide of tin, SnS^2, which is readily soluble in alkaline sulphides, less readily in caustic alkalis; and by ignition in the air, is converted into binoxide.

There is no difficulty in detecting stannous salts in presence of stannic salts; the reactions with terchloride of gold and chloride of mercury, and the brown colour of the sulphide, SnS, are sufficient to detect even the smallest traces of stannous oxide.

SULPHIDES OF TIN.—The sulphide of tin, SnS, corresponding to the protoxide, does not possess acid properties, and does not combine with alkaline sulphides to form sulpho-salts. It is true that it is dissolved by digestion with an alkaline sulphide, but this is in consequence of its conversion into bisulphide, which is precipitated on the addition of hydrochloric acid. Bisulphide of tin, SnS^2, does combine with alkaline sulphides, forming sulphostannates.

Blowpipe reactions.—All tin compounds, when heated on charcoal with carbonate of sodium and cyanide of potassium, yield a malleable metallic globule, without any incrustation on the charcoal. This globule, when dissolved in hydrochloric acid, gives a white precipitate with chloride of mercury, which becomes grey when heated.

Separation of Tin from Arsenic.—Tin is distinguished from arsenic and antimony by its forming no gaseous compound with hydrogen, so that no metallic deposit can be obtained from a tin compound by means of Marsh's apparatus. Hence the presence of arsenic in metallic tin is readily detected by treating the granulated metal with sulphuric acid (without zinc) in Marsh's apparatus. In a mixture of the sulphides of arsenic and tin, the arsenic is volatilised with a garlic smell when the sulphides are heated before the blowpipe on charcoal with carbonate of sodium and cyanide of potassium, while a malleable metallic globule of tin is left, without any incrustation on the charcoal. Or the sulphides may be dissolved in hydrochloric acid and chlorate of potassium, and the solution, after expelling by heat the excess of chlorine, tested by Marsh's apparatus. A complete and accurate separation of tin from arsenic is effected by heating their sulphides or oxides in a stream of hydrosulphuric acid, when the sulphide of arsenic volatilises entirely, while the sulphide of tin remains behind. The sulphide of arsenic is collected in aqueous ammonia, the solution saturated with hydrochloric acid, which reprecipitates the sulphide, which is then oxidised by the addition of chlorate of potassium and heating, without filtration; and the arsenic acid thus formed, precipitated as arsenate of magnesium and ammonium, dried and weighed. The sulphide of tin is converted into binoxide by ignition in the air, and weighed.

Separation of Tin from Antimony.—Tin is detected in presence of antimony by oxidising the two metals, or their sulphides, by nitric acid, and boiling the oxides (after thoroughly washing them) with tartaric acid, which dissolves the oxide of antimony alone; the residual binoxide of tin is reduced to the metallic state by fusion with cyanide of potassium and carbonate of sodium, dissolved in hydrochloric acid, and tested with chloride of mercury. Or both the oxides may be reduced to a metallic globule by fusion with cyanide of potassium and carbonate of sodium, and the globule heated on charcoal in the inner blowpipe flame when the antimony is volatilised, forming a white incrustation on the charcoal, while a malleable globule of tin remains behind. An accurate quantitative separation of tin and antimony can only be effected by the process described in the following section.

Separation of Tin from Arsenic and Antimony.—A qualitative separation of these metals may be effected by digesting the freshly precipitated mixed sulphides with a solution of carbonate of ammonium, which dissolves all the sulphide of arsenic together with a little of the sulphide of tin. The arsenic is detected by reprecipitating the sulphide from this solution by hydrochloric acid, and reducing it by heating with cyanide of potassium in a stream of carbonic anhydride; or dissolving it in as little aqua-regia as possible, and testing the solution by Marsh's process. The sulphides insoluble in carbonate of ammonium are dissolved in hydrochloric acid to which a little chlorate of potassium has been added, and the solution treated with zinc and sulphuric acid in a small Marsh's apparatus; when the antimony is detected by the metallic deposit obtained, which must be identified by the reactions given above. The tin is found in the Marsh's apparatus as a black metallic powder, which is separated by levigation from the undissolved zinc, dissolved in hot hydrochloric acid, and the solution tested with chloride of mercury.

The only process by which a complete quantitative separation can be effected, is that given by H. Rose, which is founded on the insolubility of metantimonate of sodium. The mixed sulphides are oxidised by nitric acid, evaporated to dryness in a water-bath, and the residue fused in a silver crucible with eight times its weight of solid caustic soda. The fused mass, when cool, is digested in hot water until the undissolved portion is in the form of a finely divided powder: about $\frac{1}{3}$ its volume of alcohol added to the solution, and the whole allowed to stand for twenty-four hours, with occasional stirring. The precipitate, which contains all the antimony as metantimonate of sodium, is then filtered off, and washed successively with mixtures containing 3 vols. water and 1 vol. alcohol, 1 vol. water and 1 vol. alcohol, and 1 vol. water and 3 vols. alcohol, to which a little carbonate of sodium has been added: the washing is continued as long as hydrosulphuric acid gives the slightest yellow colour with the wash-water. The alcoholic filtrate, which contains all the arsenic and tin as arsenate and stannate of sodium, is saturated with hydrochloric acid, which produces a copious precipitate: and the acid solution, in which the precipitate is suspended, is saturated with hydrosulphuric acid, and the precipitated sulphides filtered off. The filtrate is heated till all the alcohol and free hydrosulphuric acid are expelled, treated with sulphurous acid, and again saturated with hydrosulphuric acid, which generally precipitates a little more tersulphide of arsenic. The mixed sulphides of arsenic and tin are then heated in a current of hydrosulphuric acid, as described page 97, and the arsenic estimated as arsenate of magnesium and ammonium, $AsO^4Mg^2NH^4 + \frac{1}{2}H^2O$, and the tin as binoxide. The precipitate of metantimonate of sodium is dissolved in a mixture of hydrochloric and tartaric acids, and the antimony precipitated as sulphide from the acid solution by hydrosulphuric acid. The composition of the sulphide not being constant, the antimony cannot be determined directly from the weight of the sulphide. To estimate the antimony, a weighed portion of the sulphide is oxidised by nitric acid, until all the sulphur is converted into sulphuric acid, which is then precipitated by chloride of barium, and the antimony calculated from the weight of sulphate of barium obtained. Or a weighed portion of the sulphide is reduced by heating in a stream of hydrogen, and the residual metallic antimony weighed. Or the sulphide may be converted into Sb^4O^8 by ignition with oxide of mercury, and weighed in that form.

This process gives accurate results when carefully performed: but it is difficult to avoid loss from spirting during the fusion with soda, a process which is also injurious to the silver crucible. To obviate these inconveniences, Dr. Williamson has proposed to employ hypochlorite of sodium to oxidise the sulphides, instead of soda. The sulphides are dissolved in as little sulphide of sodium as possible, enough soda added to neutralise exactly all the acids that will be formed, and the whole boiled with excess of hypochlorite of sodium. Or chlorine may be passed at once into the hot alkaline solution, until complete oxidation be effected. When performed with care, this method of oxidation is perfectly satisfactory.

Vohl (Ann. Ch. Pharm., xcvi. 237) states that tin may be separated from arsenic and antimony by treating their hydrochloric acid solution with hyposulphite of sodium; when antimony and arsenic are completely precipitated as sulphides, while all the tin remains in solution.

4. **Gold.** Au. Atomic weight, 196.

Gold is generally found native; occasionally in combination with other metals. It is a soft, yellow, very heavy metal, combining with oxygen with great difficulty. It is insoluble in hydrochloric, sulphuric, or nitric acid: (nitric acid containing nitrous acid dissolves it slightly:) it is soluble in aqua-regia, forming a solution of terchloride of gold, $AuCl^3$. Finely divided gold is dissolved with ease by gaseous chlorine or chlorine-water.

OXIDES OF GOLD. *Protoxide*, Au^2O. *Teroxide*, Au^2O^3.

a. *Protoxide of Gold. Aurous Oxide.* Au^2O.— A dark violet or black powder, which separates on the addition of a small quantity of subnitrate of mercury to terchloride of gold. It is insoluble in oxygen acids: soluble in aqua-regia: hydrochloric acid decomposes it into terchloride and metallic gold. Its corresponding chloride, AuCl, is similarly decomposed by water. On ignition aurous oxide loses its oxygen, leaving metallic gold.

b. *Teroxide of Gold. Auric Oxide.* Au^2O^3.— A brownish-black powder, which very readily parts with its oxygen when heated. It is insoluble in nitric or sulphuric acid, unless very concentrated, and then but very slightly soluble: hydrochloric acid dissolves it readily, forming terchloride. A solution of terchloride of gold gives, with *hydrosulphuric acid*, a dark brown precipitate of tersulphide, Au^2S^3, soluble in aqua-regia, in sulphide of ammonium (with difficulty), insoluble in nitric acid. *Caustic potash* gives no precipitate, unless it contains organic matter, when it separates some protoxide (Rose): *ammonia* gives a reddish-yellow precipitate of fulminating gold. Gold is reduced from a solution that does not contain free nitric acid, by most other metals, even by platinum, silver, and mercury. The same reduction is effected more readily by the following reagents, especially on heating: *protosalts of iron* (when excess of hydrochloric acid must be present, to prevent the formation of an insoluble basic iron-salt), a hydrochloric acid solution of *arsenious acid, terchloride of antimony, sulphurous acid, oxalic acid,* a solution of *sugar* in potash, and many other organic substances. ($AuCl^3 + 3SO^4Fe^2 = Au + S^3O^{12}Fe^4 + Fe^2Cl^3$; $2AuCl^3 + 3C^2O^4H^2 = Au^2 + 6CO^2 + 6ClH$.) The reduced gold is generally precipitated as a brown or reddish-purple powder, which assumes a yellow metallic appearance when rubbed with any hard substance. (c) A solution of *chloride of tin*, to which enough hydrochloric acid has been added to form a clear solution, gives a purple colour or precipitate, even in the most dilute gold solution; this precipitate (purple of Cassius) is insoluble in hydrochloric acid, but, when freshly precipitated, is soluble in ammonia, forming a purple solution.

Blowpipe reactions. — When heated on charcoal with borax or carbonate of sodium in the inner flame, gold compounds yield a yellow, very malleable globule of metallic gold.

Separation and estimation of Gold. — The detection of gold is attended with no difficulty, owing to the ease with which it is reduced to the metallic state. In many cases the reduction is quite complete, as for instance with protosalts of iron; so that this reagent is generally employed for the estimation of gold. In the analysis of a solution containing gold and other metals, it is better to remove the gold by protosulphate of iron before passing hydrosulphuric acid: otherwise, owing to the imperfect solubility of sulphide of gold in sulphide of ammonium, some difficulty may arise in its subsequent detection. In the analysis of ores which contain very little gold (*e.g.* pyrites), the gold is removed by digestion with chlorine-water (or chloride of lime and hydrochloric acid), and precipitated from the concentrated solution by arsenious acid. Silver coins frequently contain traces of gold, which are left as a black powder when the coin is dissolved in nitric acid. Gold may also be separated from silver and copper by boiling in concentrated sulphuric acid.

5. **Platinum.** Pt. Atomic weight, 99.

Is found both native and in combination with other metals. It is a grey, soft, very heavy metal, whose tendency to combine with oxygen is even less than that of gold. When pure it is not at all attacked by nitric, hydrochloric, or sulphuric acids: when alloyed with other metals (*e. g.* silver), it is somewhat soluble in nitric acid. Aqua-regia dissolves it, forming bichloride of platinum, $PtCl^2$. Platinum is not fusible at the strongest heat of a furnace. When heated with caustic alkalis it is attacked and oxidised: and when heated with easily reducible metallic oxides (*e. g.* oxide of lead) it forms an easily fusible alloy with the reduced metal. Substances of this kind, therefore, must not be fused in platinum crucibles.

Oxides of Platinum. *Protoxide*, Pt^2O. *Binoxide*, Pt^2O^2.

a. *Protoxide of Platinum. Platinous Oxide.* Pt^2O.—Its hydrate is precipitated as a black powder by potash from a solution of protochloride of platinum, PtCl. When ignited it is first converted into the anhydrous oxide, and then into metallic platinum, giving off oxygen. The protochloride is obtained by heating the bichloride, $PtCl^2$: it is a brown powder, which, when free from bichloride, is insoluble in water: hydrochloric acid dissolves it, without access of air, as PtCl; with access of air, as $PtCl^2$. Protochloride of platinum is soluble in potash or soda: alcohol precipitates the whole of the platinum from this solution in a finely divided state (platinum-black). The solution of protochloride of platinum is dark-brown. Its most characteristic reaction is with *ammonia*, with which it gives a green crystalline precipitate of $PtClNH^3$, insoluble in cold water or alcohol: the supernatant liquid is colourless.

b. *Binoxide of Platinum. Platinic Oxide.* Pt^2O^2.—Its hydrate is precipitated with a reddish-brown colour on the first addition of potash to nitrate of platinum. When ignited it loses water and then oxygen, leaving metallic platinum. The corresponding chloride, $PtCl^2$, is obtained by dissolving platinum in aqua-regia, and driving off the excess of acid by heat: towards the end of the operation a water-bath must be used, since the bichloride is decomposed at a higher temperature, with formation of protochloride. It is a dark-brown syrupy liquid, readily soluble in water and alcohol, forming a reddish yellow solution, which, if any protochloride be present, has a dark-brown colour. (c) *Ammonia* and *potash* give with an *acid* solution of bichloride of platinum (with a *neutral* solution chloride of ammonium or potassium must be used), a yellow crystalline precipitate of chloroplatinate of ammonium, $PtCl^3NH^4$, or of potassium, $PtCl^3K$. These precipitates are insoluble in acids, but soluble in excess of alkali: the solution of chloroplatinate of ammonium in ammonia gives a white precipitate with hydrochloric acid: they are almost insoluble in water, quite insoluble in alcohol. They serve for the detection and separation of platinum, as well as of potassium and ammonium. The chloroplatinate of ammonium is converted by ignition into spongy platinum: platinum is always estimated in this form. The chloroplatinate of potassium is not entirely reduced by ignition: but when heated with oxalic acid or in a stream of hydrogen, it is completely decomposed into chloride of potassium (which may be dissolved out by water), and spongy platinum. *Sodium* forms an analogous compound, $PtCl^3Na$, which is soluble in water. *Iodide of potassium* gives a dark red solution, whence biniodide of platinum, PtI^2, separates on heating. *Hydrosulphuric acid* gives a dark brown precipitate of bisulphide of platinum, Pt^2S^2, which forms very slowly: it is soluble in sulphide of ammonium and aqua-regia, insoluble in nitric acid. *Chloride of tin* gives a dark brown-red colour, but no precipitate. Platinum is not so easily reduced from its salts as gold is. *Protosalts of iron* do not reduce terchloride of platinum, neither does *oxalic acid: formic acid* reduces metallic platinum on heating, if the free acid be neutralised with carbonate of sodium.

Blowpipe reactions.—All platinum compounds are reduced to spongy platinum in the inner flame, giving no coloured beads with borax or microcosmic salt. The spongy platinum cannot be fused into a globule before the blowpipe.

Separation and estimation of Platinum.—Platinum is separated from most other metals by its absolute insolubility in nitric or hydrochloric acid. From *gold* it is readily distinguished and separated by its reaction with chloride of ammonium or potassium. Since hydrosulphuric acid precipitates platinum very slowly, it is better, in analysing a solution containing platinum and other metals, to remove the platinum by chloride of potassium before passing hydrosulphuric acid.

6. **Iridium.** Ir. Atomic weight, 98·6.

Is always found in platinum-ores. It resembles platinum in appearance: is even more difficultly fusible than platinum: is insoluble in nitric, hydrochloric, or sulphuric acid, or in aqua-regia. If it be alloyed with excess of platinum, aqua-regia dissolves it to a certain extent.

OXIDES OF IRIDIUM.—There are four oxides of iridium, of which the most important is the *binoxide*, Ir^2O^2. The corresponding bichloride, $IrCl^2$, is prepared by dissolving in aqua-regia the black powder (sesquioxide of iridium, Ir^4O^3), obtained by igniting the metal with nitrate of potassium, or hydrate and chlorate of potassium. The bichloride is also formed when a mixture of iridium and chloride of sodium is gently heated in a current of chlorine: if iridium alone is heated in chlorine, protochloride, IrCl, is formed. The aqueous solution of bichloride of iridium has a dark brownish-red colour. With *potash*, it gives a reddish-brown precipitate of chloriridate of potassium, $IrCl^3K$, soluble in excess of potash to a light-green solution, which, when heated, becomes first colourless, then red, and finally violet-blue, and a blue precipitate of hydrated binoxide of iridium separates gradually as the solution is evaporated. The colourless potash solution is reduced when heated with alcohol, finely divided iridium being precipitated. With *chloride of ammonium*, it gives a brownish-red precipitate of chloriridate of ammonium, $IrCl^3NH^4$, and a colourless solution, which is coloured blue by heat or by exposure to the air. With *nitrate of silver* it gives a dark-blue precipitate, which rapidly becomes colourless: this is a compound of sesquichloride of iridium and chloride of silver, $Ir^2Cl^6Ag^3$. With *subnitrate of mercury*, a brownish-yellow precipitate of $Ir^2Cl^6Hg^6$. *Hydrosulphuric acid* decolorises bichloride of iridium, separating sulphur, and forming sesquichloride of iridium, whence brown bisulphide, Ir^2S^2, gradually separates. Chloriridate of ammonium is converted by hydrosulphuric acid into soluble sesquichloriridate, $Ir^2Cl^6(NH^4)^3$. When terchloride of iridium is heated with formic acid, metallic iridium is slowly reduced.

For the separation of iridium from *platinum*, *see* article Platinum-ores, in Part IV. p. 237.

7. **Wolfram** or **Tungsten.** W. Atomic weight, 92.

Occurs in nature as tungstic acid, tungstate of iron and manganese (wolfram), and tungstate of calcium (tungsten). It is a very heavy, hard, and difficultly fusible metal: at the ordinary temperature it is not affected by exposure to the air, but at a red heat it is oxidised into tungstic anhydride, W^2O^3. Its behaviour to acids is as yet imperfectly known.

OXIDES OF WOLFRAM. *Tungstic oxide*, W^2O^2. *Tungstic anhydride*,

W^2O^3.—There is another oxide, W^4O^5, intermediate between these two oxides: it is of a blue colour, and is generally spoken of as the blue oxide. Some regard it as a tungstate of wolfram: apparently it is a compound of tungstic anhydride and tungstic oxide. All lower oxides of wolfram are converted into tungstic anhydride by heating in the air or with nitric acid.

a. *Tungstic Oxide. Brown Oxide of Wolfram.* W^2O^2.—A brown powder, insoluble in acids or alkalis, obtained by heating tungstic anhydride in a stream of hydrogen, or by fusing tungstate of potassium with chloride of ammonium.

b. *Tungstic Anhydride*, W^2O^3.—A soft, lemon-yellow powder, not volatile at any heat, insoluble in water and acids. It combines with water, forming a white compound, $W^2O^4H^2$, which possesses acid properties. This is *tungstic acid:* it combines with basic metals, forming a class of salts called tungstates. The alkaline tungstates are soluble in water: those of the other metals are insoluble. Tungstic acid is precipitated from the solution of a tungstate by nitric, hydrochloric, or sulphuric acid, and is insoluble in excess of the acid: non-volatile polybasic acids (phosphoric, tartaric) precipitate it also, but the precipitate is soluble in excess of the reagent: hence the presence of excess of phosphate of ammonium prevents its precipitation by acids. When tungstic acid or a tungstate is brought into contact with hydrochloric, sulphuric, phosphoric, or acetic acid, and metallic *zinc*, a deep-blue colour is produced, owing to the reduction of tungstic acid to the blue oxide. *Hydrosulphuric acid* does not precipitate sulphide of wolfram from an acid solution, but produces a blue colour, owing to the formation of the blue oxide. *Sulphide of ammonium* does not precipitate a solution of an alkaline tungstate, till hydrochloric acid is added, when brown bisulphide, W^2S^2, is precipitated, and the solution is coloured blue. Sulphide of wolfram is soluble in sulphide of ammonium. *Chloride of tin* gives with an alkaline tungstate a yellow precipitate, which, on addition of hydrochloric or sulphuric acid, and gentle heating, becomes blue. If excess of the tin-salt be used, the colour is greenish. *Subnitrate of mercury* gives a yellowish-white precipitate, which is blackened on the addition of ammonia.

Blowpipe reactions.—Tungstic acid is not changed when heated alone in the oxidising flame: in the reducing flame it is blackened. With *borax* all oxides of wolfram give a colourless bead in the outer flame: in the inner flame, a yellow bead, which becomes darker on cooling. With *microcosmic salt* they give a colourless bead in the outer flame: in the inner flame, a blue bead, which the presence of iron changes to a blood-red. The addition of tin changes the red bead to blue or green. When heated on charcoal with carbonate of sodium and cyanide of potassium, they are reduced, and the wolfram may be separated as a grey metallic powder by levigating the charcoal.

Separation and estimation of Wolfram.—For the analysis of the mineral wolfram, or any other insoluble tungstate, the substance is reduced to an impalpable powder, and digested with aqua-regia till it is completely decomposed, evaporated to dryness in the water-bath, and the metallic chlorides formed dissolved out with acidulated water. The residual tungstic acid (which also contains a little silicic and niobic acids) is washed with alcohol, and treated with ammonia, which dissolves the tungstic acid, leaving the silicic and niobic acids undissolved. These are filtered off, the filtrate evaporated and ignited, when pure tungstic anhydride is obtained. Another method is to fuse three parts of the finely powdered mineral with two parts of carbonate, and half a part of nitrate of potassium in a platinum crucible, by which process the tungstic acid is entirely converted into tungstate of potassium, which is dissolved out by water, and separated by filtration from the insoluble oxides. The filtrate is nearly neutralised with nitric acid, and precipitated by subnitrate of mercury, a few drops of ammonia being added to neutralise the free nitric acid. The precipitate is thoroughly washed, (first with water, and lastly with a very dilute solution of subnitrate of mercury), and ignited, when tungstic anhydride is obtained. Insoluble tungstates may also be decomposed by heating with concentrated sulphuric acid, or by fusion with acid sulphate of potassium.

Wolfram is always estimated as tungstic anhydride, in which form it is usually separated.

8. **Molybdenum.** Mo. Atomic weight, 48.

Occurs in nature principally as sulphide of molybdenum and as molybdate of lead. It is a silver-white metal, very difficultly fusible, and slightly malleable. It is not affected by exposure to the air at the ordinary temperature: but when heated in contact with air it becomes first brown, then blue, and finally white, passing through various stages of oxidation till it is converted into molybdic anhydride, Mo^2O^3. It is insoluble in hydrochloric acid: nitric acid or aqua-regia convert it into molybdic acid if sufficient nitric acid be present; if not, nitrate of molybdenum is formed.

OXIDES OF MOLYBDENUM. *Protoxide*, Mo^2O. *Binoxide*, Mo^2O^2. *Molybdic Anhydride*, Mo^2O^3.—The oxides of molybdenum correspond with those of wolfram. There is also a blue oxide of molybdenum, Mo^4O^5, intermediate between the binoxide and the anhydride.

a. *Protoxide of Molybdenum. Molybdous Oxide.* Mo^2O.—A black powder, obtained by digesting molybdic anhydride with a quantity of hydrochloric acid not sufficient to dissolve it, and with metallic zinc. It is insoluble in acids. The hydrate, MoHO, is formed when an alkaline molybdate is dissolved in hydrochloric acid and reduced by zinc. It is a black powder, soluble in acids, forming *molybdous salts.* It absorbs oxygen readily from the air: when heated in contact with air it takes fire, and is converted into molybdic anhydride. When heated out of contact with the air it is converted into molybdous oxide, insoluble in acids.

b. *Binoxide of Molybdenum. Molybdic Oxide. Brown Oxide.* Mo^2O^2.—A brown powder, obtained by fusing an alkaline molybdate with chloride of ammonium, and treating the fused mass with water: or by reducing molybdic anhydride by hydrogen, at a moderate temperature. It is insoluble in acids. The hydrate is precipitated by ammonia from an aqueous solution of bichloride of molybdenum. It is also brown, soluble in acids, forming *molybdic salts:* slightly soluble in water. By ignition out of contact with the air, it is converted into molybdic oxide.

Molybdous and molybdic salts resemble each other very closely in their reactions. Both form dark-brown solutions, which become blue on exposure to the air, from which sulphide of molybdenum is slowly precipitated by *hydrosulphuric acid.* The best reagent for distinguishing them is *carbonate of potassium*, which precipitates the hydrate both from molybdous and molybdic salts; but in the former case the precipitate is difficultly soluble in excess of the reagent, while in the latter it is readily soluble. Both the lower oxides of molybdenum, as well as the sulphide, are converted into molybdic anhydride by ignition in the air.

c. *Molybdic Anhydride*, Mo^2O^3. — A white crystalline powder, slightly soluble in water, soluble in acids and in alkalis. When ignited in a covered vessel, it fuses to a yellow liquid, which on cooling forms a light yellow crystalline mass, much less soluble in acids than before ignition. When heated in the air it sublimes at no very high temperature into crystalline needles. It combines with water, forming a white compound, $Mo^2O^4H^2$, which has acid properties. This is *molybdic acid:* it is bibasic, and combines with metals, forming a class of salts called *molybdates.* The alkaline molybdates are soluble in water: most others are insoluble. Nitric or hydrochloric acid precipitates molybdic acid from a solution of a molybdate; the precipitate is soluble in excess of acid. Metallic zinc immersed in the hydrochloric acid solution, produces a blue colour, which gradually becomes green, and finally dark-brown, owing to the reduction of the molybdic acid to molybdous hydrate, which remains dissolved in the hydrochloric acid. *Hydrosulphuric acid* gradually precipitates sulphide of molybdenum from an acid solution of molybdic acid: the supernatant liquid has a blue or green colour. The same precipitate is produced when an aqueous solution of an alkaline molybdate is saturated with sulphide of ammonium or hydrosulphuric acid, and hydrochloric acid added to it. *Chloride of tin* gives with an alkaline molybdate a greenish-blue precipitate, which hydrochloric acid dissolves to a green solution: if very little chloride of tin be used, the solution is blue. *Subnitrate of mercury* gives a yellowish precipitate, soluble in nitric acid, blackened by ammonia. (c) When molybdate of ammonium is mixed with a small quantity of a *phosphate* or *arsenate*, excess of nitric acid added, and the whole heated, a yellow solution and a yellow precipitate are formed (p. 60).

Blowpipe reactions. — Molybdic anhydride, when heated on charcoal in the outer flame, is volatilised, and forms a white crystalline sublimate on the charcoal; in the inner flame, it may be reduced (even without carbonate of sodium) to metallic molybdenum, which is separated as a grey powder on levigating the charcoal. With *borax* all oxides of molybdenum give, in the outer flame, a bead which is yellow when hot, and colourless on cooling: in the inner flame, a dark-brown bead, which is opaque if excess of molybdenum be present. By long continued heat the molybdic oxide may be separated as dark-brown flakes, swimming in a clear yellow glass. With *microcosmic salt*, in the outer flame, all oxides of molybdenum give a bead which is greenish when hot, and colourless on cooling: in the inner flame, a clear green bead, from which molybdic oxide cannot be separated by continued heat.

Separation and estimation of Molybdenum.—For the extraction of molybdic acid from minerals, various processes are employed. Sulphide of molybdenum (molybdenite) is converted into molybdic anhydride by ignition in an open crucible, placed in a slanting position over the lamp, the anhydride is then dissolved out with ammonia. If the sulphide in lumps is heated in an open glass tube, through which a stream of air is drawn by an aspirator, molybdic anhydride sublimes in crystals in a state of perfect purity. (Wöhler. Ann. Ch. Pharm., c.) Molybdate of lead is finely powdered, and freed from carbonates of zinc, iron, and calcium by digestion with dilute hydrochloric acid, and thoroughly washed by decantation. It is then heated with 1¼ part concentrated sulphuric acid, with constant stirring, till it is perfectly white, and the sulphuric acid begins to evaporate. It is then allowed to cool, and a considerable quantity of water added, and the sulphate of lead which remains insoluble filtered off. The filtrate is mixed with nitric acid, and evaporated with constant stirring in a porcelain basin, till the sulphuric acid begins to evaporate, when the molybdic acid separates as a white powder: it is freed from phosphoric acid by washing with water, to which at the last a few drops of nitric acid have been added. Or the mineral, after treatment with dilute hydrochloric acid, may be evaporated to dryness with strong hydrochloric acid: the dry residue (containing basic chloride of lead and molybdic acid) is exhausted with ammonia, and the ammoniacal solution crystallised, or evaporated as before with nitric acid, and treated with water. Or the mineral is fused with its own weight of calcined tartrate of potassium, the fused mass exhausted with water, and the aqueous solution evaporated to dryness after saturation with nitric acid. The nitrate of potassium is dissolved out of the residue with water, and molybdic acid remains behind. For the estimation of molybdenum, the molybdic acid is dissolved in dilute ammonia, and the solution precipitated by subnitrate of mercury: the precipitate is thoroughly washed with a dilute solution of the subnitrate, dried, and ignited at a moderate heat in a stream of hydrogen, when it is reduced to brown binoxide of molybdenum, Mo^2O^2, and weighed in that form.

There is so close a resemblance between the reactions of molybdenum and wolfram compounds, that their distinction is attended with some difficulty. Molybdic acid is distinguished from tungstic acid by its fusibility and volatility, and by its solubility in excess of acid when precipitated by nitric or hydrochloric acid from an alkaline solution. For the separation of the two acids Rose gives the following method. Tartaric acid is added to the alkaline solution of the two acids, and the whole saturated with hydrochloric acid. The molybdenum is then precipitated as sulphide by repeated saturation with hydrosulphuric acid (a long and difficult process), the sulphide filtered off, and gently ignited in a stream of hydrogen till it no longer loses weight. It is then in the form of bisulphide, Mo^2S^2, and is weighed as such. The filtrate is evaporated to dryness and the residue ignited in the air: if the residue be at all black (owing to the carbon of the tartaric acid not being entirely burnt) it must be fused with a little nitrate, and excess of carbonate, of potassium. The fused mass is dissolved in water, the tungstic acid precipitated by subnitrate of mercury, ignited, and weighed. The same process which effects the separation of *antimony* from arsenic and tin, serves also for its separation from wolfram and molybdenum, the alkaline tungstates and molybdates being soluble in water. From *arsenic* they are separated by converting the arsenic into arsenic acid, and precipitating it by a magnesium-salt.

9. **Vanadium.** V. Atomic weight, 68·5.

Occurs as vanadate of lead in the brown lead-ore from Zimapan: in small quantities in many iron- and copper-ores, and in the slags from blast-furnaces. It is a white hard metal, that may be reduced to an iron-grey powder. It is not oxidised by exposure to moist air at the ordinary temperature, but acquires a reddish tint. Heated in the air it burns vividly, and is converted into black oxide, V^2O^2. It is not attacked by sulphuric, hydrochloric, or hydrofluoric acid: nitric acid and aqua-regia dissolve it readily, forming a light-blue solution.

OXIDES OF VANADIUM. *Protoxide*, V^2O. *Binoxide*, V^2O^2. *Vanadic Anhydride*, V^2O^3. — Like wolfram and molybdenum, vanadium forms one or more oxides intermediate between V^2O^2 and V^2O^3, which are soluble in water with a blue, green, or orange-red colour.

a. *Protoxide of Vanadium. Vanadous Oxide.* V^2O.—A black powder, obtained by heating vanadic anhydride in a stream of hydrogen. When heated in the air it is converted into binoxide. It does not combine either with acids or alkalis; but on digestion with nitric acid or potash it absorbs oxygen and is dissolved, in the former case giving a light blue solution, in the latter, a solution of vanadate of potassium.

b. *Binoxide of Vanadium. Vanadic Oxide. Vanadous Anhydride.* V^2O^2. — A black earthy powder, obtained by heating vanadium or the protoxide in contact with air. It is slowly but perfectly soluble in acids, forming *vanadium-salts;* their solutions are blue, and by exposure to the air absorb oxygen and become green. It is also soluble in fixed alkalis, forming *vanadites.* Vanadium-salts give the following reactions. *Hydrosulphuric acid* gives no precipitate in a neutral or acid solution.* *Sulphide of ammonium* gives a black-brown precipitate, soluble in excess to a dark purple-red solution, whence brown sulphide of vanadium is precipitated by a dilute acid. *Ferrocyanide of potassium* give a yellow precipitate, insoluble in acids, which turns green by exposure to the air. *Gallic acid* gives a black precipitate, which settles slowly, leaving a bluish solution. The *fixed alkalis* and *their normal carbonates* give a greyish-white precipitate of hydrate, soluble in moderate excess, reprecipitated by a large excess as an alkaline vanadite. *Ammonia* gives a brown precipitate, somewhat soluble in water, insoluble in water containing ammonia.

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* Though vanadium, like wolfram, is not precipitated from an acid solution by hydrosulphuric acid, it is nevertheless included in this group, because its sulphide is soluble in sulphide of ammonium, forming a sulpho-salt, and is precipitated from this solution by hydrochloric acid.

Only the alkaline *vanadites* are soluble in water. Their solution gives with *sulphide of ammonium* a fine purple-red colour, owing to the formation of a soluble sulpho-salt. By *acids* they are coloured blue, owing to the formation of a double salt of vanadium and the alkaline metal. Insoluble vanadites, when moistened with water, rapidly become green, being converted into vanadates.

c. *Vanadic Anhydride*, V^2O^3. — A red powder, obtained by the ignition of vanadate of ammonium. It is fusible, non-volatile, and does not lose oxygen at a white heat. It is slightly soluble in water: the solution, which contains *vanadic acid*, reddens litmus strongly. It dissolves both in acids and alkalis, in the former case forming *vanadic salts*, in the latter, *vanadates*. Its solution in acids is generally red or yellow: it is very easily reduced by *hydrosulphuric*, *sulphurous*, or *oxalic acid*, *sugar*, *alcohol*, and many other organic compounds, the solution being coloured blue. *Sulphide of ammonium* precipitates brown sulphide, soluble in alkaline sulphides, or caustic alkalis, to a purple-red solution, whence light-brown sulphide of vanadium is precipitated by dilute acids. *Ferrocyanide of potassium* gives a green precipitate, insoluble in acids.

Vanadates are mostly soluble in water, all in nitric acid. Alkaline vanadates are difficultly soluble in water containing free alkali or an alkaline salt: thus vanadate of ammonium is insoluble in a saturated solution of chloride of ammonium. Aqueous solutions of vanadates are coloured red by stronger acids, but the colour frequently disappears after a time. *Hydrosulphuric acid* in *neutral* solutions gives a mixed precipitate of sulphur and bihydrate of vanadium: in *acid* solutions, it separates sulphur and gives a blue solution. *Sulphide of ammonium* behaves as with vanadic salts. *Terchloride of antimony*, *lead-salts*, *protosalts of copper* and of *mercury*, give orange-red precipitates. Vanadates of a fixed base are not decomposed by heat.

Blowpipe reactions.— When vanadic anhydride is heated on charcoal in the inner flame, it is reduced to protoxide. With *borax* and *microcosmic-salt*, all oxides of vanadium give in the outer flame a clear colourless bead, which is yellowish if a large amount of the vanadium compound be present: in the inner flame a green bead, which, if a large amount of the vanadium compound be present, is brown while hot, and becomes green on cooling. On heating the green bead in the outer flame, it becomes colourless or slightly yellow. A blue bead cannot be obtained before the blowpipe with an oxide of vanadium.

Separation and estimation of Vanadium. — To extract vanadium from iron-ore, the powdered mineral is fused for an hour at a red heat with one third its weight of nitrate of potassium, the fused mass when cool boiled with water and filtered. The filtrate, which is yellow, contains vanadate, chromate, phosphate, nitrite, and silicate of potassium and aluminium: it is *nearly* neutralised with nitric acid, the precipitated silica and alumina filtered off, and the filtrate precipitated with excess of chloride of barium. The precipitate (of vanadate, chromate, and phosphate of barium) is washed, boiled while moist with dilute sulphuric acid, and filtered. The reddish-yellow acid filtrate is neutralised with ammonia, concentrated by evaporation, and a fragment of chloride of ammonium placed in it, when vanadate of ammonium gradually separates as a yellow crystalline powder, which, on ignition, leaves vanadic anhydride. Or the yellow solution may be at once reduced by sulphurous acid, neutralised by ammonia, the precipitated oxides digested in sulphide of ammonium, and the sulphide of vanadium precipitated from the solution by dilute sulphuric acid: fusion with nitre then converts it into vanadate of potassium.

Vanadate of lead is not completely decomposed by sulphuric acid: a complete separation is however effected by fusion with acid sulphate of potassium, and treating the fused mass with warm water, when all the lead remains as sulphate, while all the vanadium is dissolved as vanadate of potassium.

Vanadium is separated from all the preceding metals, except wolfram, by its non-precipitation by hydrosulphuric acid from an acid solution: from most of those in the next group, by the solubility of its sulphide in sulphide of ammonium.

Vanadium is estimated as protoxide, obtained by igniting vanadic anhydride in a stream of hydrogen. To obtain vanadic acid from vanadous salts, vanadite of mercury is precipitated by adding excess of chloride of mercury and then ammonia: the precipitate, after ignition, consists of vanadic acid and a little oxide of mercury, from which it is freed by solution in carbonate of ammonium. From vanadates vanadic anhydride may be obtained by combining it with ammonia, and precipitating the vanadate of ammonium by chloride of ammonium, as above described.

10. **Tellurium.** Te. Atomic weight, 128.

Found native; also as sulphide of tellurium: also in combination with gold, silver, lead, and bismuth. Tellurium much resembles antimony in appearance, being bluish-white, brittle, and easily powdered. It is easily fusible, and may be volatilised when heated strongly out of contact with air. When heated in the air it burns with a blue flame, forming white vapours of tellurous anhydride, TeO^2. It is insoluble in hydrochloric acid: soluble in nitric acid, forming tellurous anhydride: soluble in sulphuric acid, forming an amethyst-red solution, which is decolorised by heat, and from which water precipitates metallic tellurium. Chlorine does not attack tellurium in the cold: when heat is applied, it forms either white perchloride, $TeCl^4$ or black chloride, $TeCl^2$, according to the proportions of chlorine and tellurium employed.

OXIDES OF TELLURIUM. *Tellurous Anhydride*, TeO^2. *Telluric Anhydride*, TeO^3.

a. *Tellurous Anhydride. Telluric Oxide.* TeO^2.— A white crystalline body, which separates gradually from a solution of tellurium in concentrated nitric acid. It is almost insoluble in water, acids, ammonia, or alkaline carbonates; soluble in potash and soda. When heated it melts to a yellow liquid: it may be volatilised, but requires a higher temperature than metallic tellurium. It has acid properties, combining with water to form *tellurous acid*, TeO^3H^2. This acid is precipitated as a white amorphous body, when a freshly prepared solution of tellurium in nitric acid, or when perchloride of tellurium, is treated with water. It is somewhat soluble in water, readily soluble in acids: its hydrochloric acid solution when concentrated has a yellow colour; its nitric acid solution deposits tellurous anhydride on heating. The alkaline tellurites are soluble in water, most others are insoluble; they are generally soluble in strong hydrochloric acid, and from this solution water precipitates tellurous acid, unless an excess of hydrochloric acid be present. In this reaction tellurium resembles antimony and bismuth. When a tellurite is heated with charcoal and carbonate of potassium, it is reduced to telluride of potassium, TeK^2, which produces a black stain on a moist silver plate, and is soluble in water, forming a dark red solution. When a mineral acid is added to this solution, *hydrotelluric acid*, TeH^2, is evolved, a gas resembling hydrosulphuric acid in smell, soluble in water to a pale-red solution, which on contact with the air becomes dark-red, and deposits metallic tellurium. A solution of tellurous acid in a mineral acid is precipitated by *water*. *Caustic alkalis*, and *alkaline carbonates* give a white precipitate, soluble in excess. *Hydrosulphuric acid* precipitates brown bisulphide, TeS^2, readily soluble in sulphide of ammonium. *Sulphurous acid*, or *alkaline sulphites*, give a black precipitate of metallic tellurium, especially on heating: the more concentrated the solution the more complete is the reduction. The same reduction is effected by *chloride of tin*, and metallic *zinc*.

b. *Telluric Anhydride.* TeO^3.—A yellow crystalline mass, obtained by carefully heating *telluric acid*, TeO^4H^2. It is insoluble in water, cold hydrochloric acid, boiling nitric acid, or a boiling dilute solution of potash. At a temperature very little above that required for its complete dehydration, telluric anhydride is decomposed into oxygen and tellurous anhydride. Telluric acid is prepared by fusing tellurous acid with nitrate of potassium, converting the resulting tellurate of potassium into the barium-salt, and precipitating the barium by sulphuric acid. It forms large colourless crystals, which are gradually soluble in water, insoluble in absolute alcohol: its aqueous solution is not precipitated by acids. The alkaline tellurates only are soluble in water. All tellurates may be dissolved in cold hydrochloric acid, without decomposition: the solution is not precipitated by water, as long as the least excess of hydrochloric acid is present. On boiling the solution, chlorine is evolved, and tellurous acid precipitated, which requires a considerable excess of hydrochloric acid for its solution. (Distinction of telluric from tellurous acid.) With a neutral solution of a tellurate, *chloride of barium* gives a white precipitate of tellurate of barium, soluble in nitric or hydrochloric acids. With *sulphurous* and *hydrosulphuric acids*, acid solutions of tellurates behave like those of tellurites. Tellurates also behave like tellurites when fused with charcoal and carbonate of potassium. Tellurates, when ignited, lose oxygen, and are converted into tellurites.

Blowpipe reactions.—All compounds of tellurium are easily reduced on charcoal in the inner flame; the reduced metal is volatilised, and forms a white deposit of tellurous anhydride on the charcoal. With *borax* and *microcosmic salt*, tellurous acid gives a clear colourless bead, which, heated on charcoal, is rendered grey and opaque by the reduced metal. The oxides of antimony and bismuth, when reduced on charcoal in the inner flame, give white incrustations of antimonic and bismuthic oxides, which may be confounded with tellurous anhydride. They are, however, easily distinguished in the following manner. When heated in the inner flame, antimonic oxide gives a bluish tinge, tellurous anhydride a fine green colour, to the outer flame. When heated in a tube open at both ends, tellurous anhydride volatilises entirely, forming a white sublimate on the cool part of the tube, which, by careful heating, may be fused to colourless drops. Antimonic oxide is only partially volatilised, being partly converted into non-volatile Sb^4O^8: the sublimate may be driven hither and thither in the tube by heat, but does not fuse into drops. Bismuthic oxide, when similarly treated, gives scarcely any sublimate, but melts to a dark-brown fluid, which becomes pale-yellow on cooling, and corrodes the glass.

Separation and estimation of Tellurium.—The principal minerals in which tellurium is found, are graphic and foliated tellurium, and telluride of bismuth. The two former contain, besides tellurium, gold, silver, lead, traces of other metals, and sulphur. The following are the processes adopted for the separation of the tellurium. The powdered mineral is first freed from all its constituents that are soluble in dilute hydrochloric acid, and then digested in aqua-regia, which must only contain as much nitric acid as is absolutely necessary. When the mass has become white, sulphuric and tartaric acids are added, the former to precipitate all the lead, the latter to prevent the precipitation of the tellurous acid: twice the volume of water is then added, and the sulphate of lead filtered off. The gold is then precipitated from the filtrate by protosulphate of iron, and filtered off: the filtrate concentrated, and the tellurium precipitated from it by an alkaline sulphite. Or the mineral, after treatment with dilute hydrochloric acid, is mixed with 2 parts acid sulphate of potassium, and the mixture projected by degrees into 6 parts acid sulphate of potassium, which is maintained in a state of fusion in a Hessian crucible. When the fused mass is quite white, it is poured off from the gold, which has settled at the bottom of the crucible, dissolved in water containing sulphuric acid, filtered from the sulphate of lead, the silver precipitated from the filtrate by hydrochloric acid and filtered off, and the tellurium precipitated by an alkaline sulphite. Telluride of bismuth is intimately mixed with three times its weight of calcined cream of tartar (acid tartrate of potassium), and exposed to a red heat in a closed crucible for an hour, when telluride of potassium is formed, and bismuth separated. The former is dissolved out by water which has been freed from air by boiling, and the dark-red solution gradually deposits all the tellurium on exposure to the air. Tellurium is separated from those metals whose chlorides are not volatile, by ignition in a stream of chlorine. Tellurium is separated from *arsenic*, *antimony*, and *tin* by means of an alkaline sulphite, which does not reduce any of these three metals.

11. **Selenium.** Se. Atomic weight, 79.

Found native: also as selenide of copper, iron, lead, mercury, silver, and other metals. It also occurs in many specimens of pyrites, which are used for the manufacture of sulphuric acid on a large scale; hence a seleniferous deposit is formed in the leaden chambers in which the acid is prepared. It is a brittle dark-brown metal, with a dark-grey fracture; in a finely divided state it is of a dark-red colour. It is very easily fusible, and may be drawn out into long threads, like sealing-wax : when further heated out of contact with air, it volatilises, forming a yellow vapour. When heated in the air it burns with a reddish-blue flame, forming selenous anhydride, SeO^2, and giving off a characteristic smell resembling that of horseradish. It is soluble, not very readily, in nitric acid and aqua-regia, selenous acid being formed. It is insoluble in hydrochloric and dilute sulphuric acids : concentrated sulphuric acid dissolves it, forming a fine green solution, whence water precipitates selenium as a dark-red powder. It is somewhat soluble in potash, forming a dark-red solution. When heated in a stream of chlorine, liquid chloride, $SeCl^2$, or solid perchloride, $SeCl^4$, is formed, according to the proportions of chlorine and selenium employed. When fused with metals it forms metallic selenides, closely analogous to metallic sulphides. When a metallic selenide is heated in an open glass tube, a sublimate of selenium is obtained.

OXIDES OF SELENIUM. *Selenous Anhydride*, SeO^2. *Selenic Anhydride*, SeO^3.

a. *Selenous Anhydride*, SeO^2. — Sublimes in white crystalline needles when selenium is heated in a stream of oxygen, or when a solution of selenium in nitric acid or aqua-regia is heated, after the nitric and hydrochloric acids have been distilled off. It is volatile; its vapour has no smell of horseradish. It is readily soluble in water, forming SeO^3H^2, *selenous acid*, which may be crystallised from the aqueous solution. It is also soluble in alcohol. The normal alkaline selenites are soluble in water ; most others are insoluble ; all acid selenites are soluble (Rose). Selenites are not decomposed when heated with hydrochloric acid, and no chlorine is evolved. *Hydrosulphuric acid* gives with an acid solution of a selenite (or with a solution of selenous acid), a lemon-yellow precipitate of bisulphide of selenium, SeS^2, readily soluble in sulphide of ammonium. Metallic selenium is reduced as a red powder from a solution of selenous acid or a solution of a selenite acidulated with hydrochloric acid, by *alkaline sulphites*, *chloride of tin*, metallic *zinc* and *iron :* but not by *protosulphate of iron.* The reduction is facilitated by heat, when the reduced metal becomes black. When a solid selenite is heated with chloride of ammonium out of contact with the air, a sublimate of metallic selenium is obtained.

b. *Selenic Anhydride*, SeO^3.—This compound has never been obtained. An aqueous solution of *selenic acid*, SeO^4H^2, can be obtained from the selenate of potassium which is formed by the fusion of selenium or a selenite with nitrate of potassium. Selenic acid cannot be obtained in a state of perfect purity ; for when its aqueous solution is concentrated by evaporation, it is decomposed above 280° into oxygen and selenous acid, before all the water can be driven off (Gmelin). The concentrated aqueous solution is transparent, colourless, and strongly acid. The selenates are very stable salts, and closely analogous to the sulphates. They are all soluble in water, except those of barium, strontium, calcium, and lead, which are insoluble in water or cold dilute acids. When a selenate is boiled with hydrochloric acid, chlorine is evolved, and the salt is converted into a selenite (distinction of selenic from selenous acid). Hence an indigo solution is decolorised when heated with a selenate and hydrochloric or sulphuric acid. An acid solution of a selenate is not precipitated by *hydrosulphuric* * or *sulphurous* acid, unless it has been previously decomposed by boiling with hydrochloric acid. With *nitrate of barium*, a solution of a selenate gives a white precipitate of selenate of barium, insoluble in water and dilute acids: boiling hydrochloric acid dissolves it, by decomposing it into soluble selenite. Selenates behave like selenites when heated with chloride of ammonium.

Blowpipe reactions.—All selenium compounds when heated with carbonate of sodium on charcoal in the inner flame, may be at once recognised by their characteristic smell of horseradish. They evolve the same smell when heated with microcosmic salt on charcoal. If a small quantity of a selenite or selenate be added to a clear bead of silica and carbonate of sodium, and the whole heated on charcoal in the inner flame, the bead is coloured dark-red by reduced selenium: the colour disappears on continued heating. The residue of the reduction of selenium compounds by carbonate of sodium, is selenide of sodium; if it be placed on a clean silver surface and moistened with a drop of water, a black stain is produced on the silver. Heated with acids it evolves *hydroselenic acid*, SeH^2, analogous to hydrosulphuric acid: it is an inflammable, fetid, poisonous gas, very soluble in water, from which solution metallic selenium gradually separates on exposure to the air. It precipitates selenides from many metallic salts.

Separation and estimation of Selenium.—For the analysis of the seleniferous deposit in sulphuric acid chambers, which, besides selenium, contains selenide of mercury, selenites and selenates, sulphate of lead, silica, &c., the following method is adopted:—The substance is mixed with about $\frac{1}{4}$ its weight of nitrate of potassium, and heated with a mixture of equal parts of sulphuric acid and water, till all the free nitric acid is expelled and the substance has lost its red colour. Water is then added, and the whole filtered. The filtrate (which contains all the selenium as selenites and selenates, copper, iron, mercury, and some lead) is boiled with as much chloride of sodium as amounts to half the weight of the original substance, in order to reduce the selenic to selenous acid: the solution, when cold, is poured off from the residue, and saturated with sulphurous anhydride, which separates the selenium; the separation is facilitated by boiling the solution for a short time. The mother-liquid is again boiled with hydrochloric acid, and saturated with sulphurous anhydride, when a fresh precipitate of selenium is generally obtained. The selenium thus reduced contains some iron, copper, lead, and mercury. From the three former metals it is freed by distillation, they being left behind as selenides: from the latter by solution in aqua-regia, saturation (after the free acid has been expelled) by carbonate of sodium, evaporation to dryness and ignition of the residue. The residue is then dissolved in water, boiled with hydrochloric acid, and precipitated by sulphurous acid.

The amount of selenium in selenide of lead is determined by heating the mineral in a stream of chlorine, when the selenium volatilises as chloride and perchloride, while chloride of lead remains behind. The chlorides of selenium are collected in water and saturated with chlorine, to convert all the selenous into selenic acid, which is precipitated by nitrate of barium as selenate of barium, dried, and weighed.

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* If the base of the selenate be a metal of this group, it is precipitated as sulphide by hydrosulphuric acid.

Selenium is separated together with tellurium from *arsenic*, *antimony*, and *tin*, by means of an alkaline sulphite. To separate it from *tellurium* the reduced metals are oxidised by nitric acid or aqua-regia *in excess*, excess of carbonate of sodium added, the whole evaporated to dryness, and the residue fused. It is then dissolved in water, and nitrate of barium added, when all the selenium is precipitated as selenate of barium, while tellurate of barium remains dissolved (Rose).

Group I.—Subdivision B.

1. **Lead.** Pb. Atomic weight, 103·5.

Occurs chiefly as galena, or sulphide of lead: also as carbonate and other oxygen salts, in which lead is the base. It is of a bluish-grey colour and strong metallic lustre: extremely soft and malleable. It is not affected by exposure to dry air; in moist air it becomes covered with a grey film. When heated to fusion (325°) in the air, the yellow oxide, Pb^2O, forms on the surface. Pure water in contact with air dissolves a certain portion of lead in the form of hydrate: the presence of carbonic acid in the water prevents this solution. Lead is not dissolved by hydrochloric or sulphuric acid in the cold, and very slightly on heating: nitric acid dissolves it readily, especially when somewhat dilute. Heated in chlorine, lead is converted into chloride, $PbCl$. Out of contact with air lead is volatile at a white heat.

OXIDES OF LEAD. *Oxide*, Pb^2O. *Binoxide*, Pb^2O^2.

a. *Oxide of Lead. Plumbic Oxide.* Pb^2O.—A yellow powder, which becomes somewhat darker when heated; obtained by fusing lead in contact with air, or by igniting the hydrate, carbonate, oxalate, or nitrate of lead. It is somewhat soluble in pure water; the solution is alkaline to litmus, and highly poisonous: it is insoluble in water containing carbonic acid, a sulphate, or a chloride. Its best solvents are nitric and acetic acids. Lead-salts of uncoloured acids are colourless: the solutions of normal salts redden litmus: it has a great tendency to form basic salts, whose solutions are alkaline to test-paper. *Hydrosulphuric acid* and *sulphide of ammonium* give with lead-salts a black precipitate of sulphide, Pb^2S, insoluble in dilute acids, alkalis, and alkaline sulphides, converted into sulphate by strong nitric acid. If a large excess of hydrochloric acid be present, the precipitate is reddish-brown, consisting of a mixture of sulphide and chloride of lead. Insoluble lead-salts are converted into sulphide by digestion with sulphide of ammonium, and the acid with which the lead was combined is found in the filtrate, unless it be an acid which is itself decomposed by sulphide of ammonium, *e.g.* chromic acid. *Hydrochloric acid* and soluble *chlorides* give with a not too dilute solution of lead-salts, a white precipitate of chloride, PbCl, soluble in a large quantity of water, especially on boiling, and separating from the solution on cooling in crystalline needles: it is soluble when heated with strong hydrochloric acid, less soluble in dilute hydrochloric acid, insoluble in alcohol, soluble in potash, and is not changed at all by ammonia. *Sulphuric acid* and soluble *sulphates* give, even in very dilute solutions of lead-salts, a white precipitate of sulphate, SO^4Pb^2, almost entirely insoluble in water, insoluble in cold dilute acids, soluble in boiling dilute hydrochloric acid, from which solution chloride of lead crystallises on cooling; soluble in potash, and in tartrate or acetate of ammonium with excess of ammonia, from which solution the lead is precipitated by sulphuric acid, sulphide of ammonium, or chromate of potassium: also more or less soluble in solutions of many other salts. When boiled with carbonate of sodium it is entirely converted into carbonate of lead. (c) *Iodide of potassium* gives a yellow precipitate of iodide, PbI, soluble in excess of the reagent: it is also soluble in a large quantity of boiling water, and separates on cooling in beautiful gold-yellow scales. *Cyanide of potassium* precipitates white cyanide of lead, CNPb, entirely insoluble in excess, soluble in dilute nitric acid. *Chromate of potassium* (prepared by neutralising the bichromate with ammonia) precipitates yellow chromate, $Cr^2O^4Pb^2$: soluble *phosphates*, *arsenates*, and *oxalates*, give white precipitates; all difficultly soluble in dilute nitric acid, soluble in excess of potash. *Ammonia* precipitates a white basic salt, insoluble in excess: in a solution of acetate of lead this precipitate forms slowly. *Potash* and *soda* precipitate white hydrate, PbHO, soluble in excess, especially on heating. *Alkaline carbonates* give a white precipitate of carbonate of lead, CO^3Pb^2 (white lead, ceruse), insoluble in excess. If this precipitate be formed in a hot solution it consists of a compound of hydrate and normal carbonate of lead (CO^3Pb^2+PbHO). *Ferrocyanide of potassium* gives a white precipitate of cyanide of iron and lead, Cy^3FePb^2. Metallic *iron* and *zinc* precipitate lead from its salts in the metallic state.

b. *Binoxide of Lead. Puce Oxide.* Pb^2O^2.—A dark reddish purple powder, obtained by exposing oxide of lead suspended in water to a stream of chlorine; or by digesting minium in nitric acid. *Minium*, or *red lead*, is a compound of lead and oxygen, obtained by heating the oxide in a current of air: its composition is Pb^6O^4, and it has been regarded as an intermediate oxide of lead; but with acids (which dissolve out the oxide and leave the binoxide) it behaves like a mixture of oxide and binoxide, $2Pb^2O+Pb^2O^2$. Binoxide of lead is decomposed by heat, evolving oxygen, and leaving the oxide, without any intermediate formation of minium. It does not combine with acids. Nitric acid does not dissolve it: with hydrochloric acid it evolves chlorine and forms chloride of lead: with sulphuric acid it evolves oxygen, and forms sulphate of lead. It absorbs sulphurous anhydride abundantly, forming sulphate of lead. When fused with alkalis it combines with them, forming salts which may be called *plumbates*. Binoxide of lead is precipitated together with chloride when a lead-salt is treated with hypochlorite of sodium.

Blowpipe reactions.—All lead compounds are easily reduced when heated on charcoal with carbonate of sodium, or cyanide of potassium, in the inner flame, a malleable globule of lead being obtained, and a yellow incrustation of oxide formed on the charcoal, which disappears when heated in the inner flame, colouring the outer flame blue. The oxide may be reduced by heating on charcoal without the aid of any flux. With *borax* and *microcosmic salt*, lead compounds give in the outer flame a clear yellowish bead, which is colourless when cold.

Separation and estimation of lead.—Finely powdered galena (sulphide of lead) is entirely converted into sulphate of lead by digestion in strong nitric acid: on adding water and filtering, the other metals contained in the mineral (silver, copper, iron) will be found in the filtrate. If a more dilute nitric acid be employed, a mixture of sulphate of lead and free sulphur is obtained, and some nitrate of lead is found in the filtrate. White lead (carbonate) is dissolved in nitric acid, and the lead precipitated as sulphate: if, as is often the case, the mineral contains sulphates of lead and barium, they will be left undissolved by the nitric acid, and the sulphate of lead may be separated from the residue, by digestion in tartrate of ammonium, with excess of ammonia. Chrome-yellow (chromate of lead) is first treated with a large quantity of water, to remove sulphate of calcium; then with dilute nitric acid, to remove chalk; and then with tartrate of ammonium and ammonia, to remove sulphate of lead. The residue, which consists of chromate of lead, sulphate of barium, and clay (silicate of aluminium), is digested with a mixture of fuming hydrochloric acid and alcohol, and the chlorides of lead and chromium thus formed removed by boiling in water. The insoluble residue is heated with concentrated sulphuric acid, which converts the silicate of aluminium into sulphate, which is dissolved out with water, and the alumina precipitated from the solution by ammonia. The silica is separated from the sulphate of barium, by boiling the residue in carbonate of sodium, which dissolves the silica, which may be precipitated from its solution by chloride of ammonium.

Lead is easily separated from all the metals of Subdivision A, by the insolubility of its sulphide in sulphide of ammonium. Lead is estimated either as oxide, or as sulphate. In the former case it is best to precipitate it by oxalate of ammonium from a neutral, or slightly alkaline, solution, and to convert the oxalate into oxide, by ignition in a platinum crucible. Or the lead may be precipitated as carbonate, by carbonate of ammonium and free ammonia, and converted into oxide by ignition. In the latter case, if the solution be *neutral*, the lead is best precipitated by sulphate of sodium: in an *acid* solution precipitate by free sulphuric acid, evaporate to dryness, ignite the residue till all free sulphuric acid be expelled, exhaust with water to remove any soluble salts, wash the sulphate on a filter, dry, ignite, and weigh. For precautions to be observed in igniting lead-salts, *see* p. 206.

2. **Silver.** Ag. Atomic weight, 108.

Occurs native: also as sulphide (silver-glance): as sulphide of silver and antimony (red silver ore): as chloride (horn-silver). It is a white, very lustrous metal, fusible at a somewhat lower temperature than gold. It is not oxidised by the air at any temperature: when fused in the air it dissolves oxygen, which escapes as the silver cools, giving a porous appearance to the metal. Nitric acid dissolves it readily: hydrochloric acid covers it with a thin film of chloride, which protects the metal from further attack: strong sulphuric acid dissolves it on boiling, forming sulphate of silver.

Oxide of Silver, Ag^2O.—A brown powder, obtained by precipitating nitrate of silver by potash. By ignition it is converted into metallic silver. It is rapidly soluble in nitric acid. Silver-salts of colourless acids are mostly colourless, but are gradually blackened by exposure to the air: those which are soluble in water are decomposed by heat, metallic silver being left: the aqueous solution of a normal silver-salt is neutral to test-paper. *Hydrosulphuric acid* and *sulphide of ammonium* give a black precipitate of sulphide, Ag^2S, insoluble in alkalis and alkaline sulphides, soluble in strong nitric acid. (c) *Hydrochloric acid* and soluble *chlorides* give a white curdy precipitate of chloride, ClAg, which becomes violet by exposure to the light: it is insoluble in water and dilute acids; slightly soluble in boiling concentrated nitric and hydrochloric acids; readily soluble in ammonia (reprecipitated by nitric acid); in cyanide of potassium, and hyposulphite of sodium; also soluble in saturated solutions of alkaline chlorides, whence it is reprecipitated on dilution with water. *Iodide of potassium* gives a yellowish precipitate of iodide, IAg, somewhat soluble in excess, insoluble in dilute nitric acid, almost insoluble in ammonia. *Cyanide of potassium* gives a white curdy precipitate of cyanide, CNAg, soluble in excess of the reagent, in ammonia, and in strong nitric acid. *Alkaline carbonates* give a yellowish precipitate of carbonate, *alkaline phosphates*, a yellow precipitate of phosphate, PO^4Ag^3, both soluble in ammonia and in nitric acid. *Potash* precipitates brown oxide, Ag^2O, insoluble in excess. *Ammonia*, added in very small quantity to a neutral silver solution, precipitates brown oxide, readily soluble in more ammonia: in an acid silver solution, ammonia gives no precipitate. Silver is very easily reduced from its soluble salts as a black powder: this reduction is effected (especially on heating) by many metals (*tin, iron, copper, antimony*, &c.); by *phosphorus, phosphorous acid, sulphurous acid* (imperfectly), *protosulphate* or *protacetate of iron, chloride of tin* (in excess), *formic acid*, and many other organic compounds. When reduced by organic bodies, the silver frequently forms a brilliant specular film on the sides of the vessel.

Blowpipe reactions.—All silver compounds are very easily reduced to metallic shining scales, when heated on charcoal with carbonate of sodium in the inner flame. With *borax*, silver compounds are partly reduced, even in the outer flame. With *microcosmic salt* they give a clear yellowish bead in the outer flame, which is opalescent if a large quantity of the silver compound be present: when cool, the bead is yellowish by daylight, reddish by candlelight.

Separation and estimation of Silver.—Galena frequently contains a small percentage of silver, which is extracted as follows: —The alloy of lead and silver obtained by roasting the ore, is melted in large quantities in iron basins, when on cooling the lead crystallises out, and is removed. The argentiferous residue is then exposed to the action of flame on a cupel, or basin of porous bone-earth, when the lead is oxidised and absorbed by the cupel, while the silver, not being oxidised, remains pure. Chloride of silver is reduced by contact with zinc and sulphuric acid: the reduced metal is fused into a button by heating it in a furnace with borax and carbonate of sodium. (This is a convenient method for the extraction of silver from silver residues.)

Silver is separated from almost all other metals by the insolubility of its chloride in dilute acids. From other metals which form insoluble chlorides (lead, mercury), it is separated by the solubility of its chloride in ammonia. From *lead* it is separated in the dry way by cupellation. In the wet way, the solution is largely diluted with water, heated to boiling, and precipitated by hydrochloric acid, which throws down chloride of silver only. Or the chlorides may be precipitated together, and the chloride of silver dissolved out by ammonia. Silver may also be separated from lead by cyanide of potassium, excess of which dissolves the cyanide of silver, leaving the cyanide of lead undissolved.

Silver is always estimated as chloride. For the precautions to be observed, *see* p. 204.

3. **Mercury.** Hg. Atomic weight, 100.

Occurs sometimes native, generally as sulphide (cinnabar). It is the only metal which is fluid at the ordinary temperature. It is white and lustrous; it solidifies at 40°, and boils at 360° giving off colourless vapours. It is sensibly volatile even at the ordinary temperature. It is not affected by the air at the common temperature; but when heated to a little below its boiling-point, it takes up oxygen, and is converted into the red oxide, Hg^2O. It is insoluble in hydrochloric acid: nitric acid dissolves it easily, even in the cold, forming subnitrate, NO^3Hg^2, if the mercury be in excess, and nitrate, NO^3Hg, if the acid be in excess. Aqua-regia dissolves it, forming a mixture of chloride, HgCl (corrosive sublimate), and nitrate. Boiled with excess of strong sulphuric acid, it is converted into solid sulphate, SO^4Hg^2: if the metal be in excess, and a less heat applied, subsulphate, SO^4Hg^4, is formed. When mercury is gently heated in a stream of chlorine, the chloride is formed. Mercury possesses the property of dissolving other metals, forming compounds called *amalgams*.

OXIDES OF MERCURY. *Suboxide*, Hg^4O. *Oxide*, Hg^2O.

a. *Suboxide of Mercury. Mercurous Oxide.* Hg^4O. — A black powder, obtained by precipitating a subsalt of mercury by potash. It is very difficult to obtain it perfectly pure, owing to the readiness with which it is decomposed into metallic mercury and oxide; this decomposition is induced by a slight rise in temperature, or by exposure to light. It is insoluble in water and hydrochloric acid. Its salts (*subsalts of mercury*, or *mercurous salts*) are colourless when normal: when basic, they are frequently yellow. All soluble mercurous salts are partially decomposed by water, a basic salt being precipitated and an acid salt left in solution: free acid redissolves the basic salt. *Hydrosulphuric acid* and *sulphide of ammonium* give with mercurous salts a black precipitate of subsulphide, Hg^4S, insoluble in sulphide of ammonium, or nitric acid, soluble in aqua-regia, and in sulphide of potassium. (c) *Hydrochloric acid* and soluble *chlorides* give, even in very dilute solutions, a white precipitate of subchloride, Hg^2Cl (calomel), which is insoluble in dilute acids, and is blackened by potash or ammonia. Boiling nitric acid dissolves it: boiling hydrochloric acid decomposes it into chloride, which dissolves, and metallic mercury, which remains as a grey powder. *Iodide of potassium* gives a greenish-yellow precipitate of subiodide, Hg^2I (always mixed with iodide, HgI), soluble in excess. *Cyanide of potassium* separates metallic mercury, the subcyanide being decomposed into mercury and protocyanide ($Hg^2Cy = Hg + HgCy$). *Phosphate of sodium*, *oxalic acid*, and *ferrocyanide of potassium* give white precipitates: *ferricyanide of potassium*, a reddish-brown, *chromate of potassium*, a red, *gallic acid*, a brownish-yellow, precipitate. Mercurous salts are reduced by metallic *copper* and *zinc*, *chloride of tin*, *protosulphate of iron*, *sulphurous* and *phosphorous acids*, metallic mercury being separated as a grey powder. Most subsalts of mercury are decomposed by heat: the subchloride and subbromide sublime undecomposed. All subsalts of mercury are converted into protosalts by boiling in nitric acid.

b. *Oxide of Mercury. Mercuric Oxide.* Hg^2O.—A brick-red powder, nearly black when hot, obtained by heating mercury in the air, or by carefully igniting the nitrate of mercury. When precipitated by an alkali from a mercuric salt, it has a yellow colour. It is decomposed by heat into mercury and oxygen, evolving nitrous fumes if it contains a trace of nitric acid. It is not quite insoluble in water: readily soluble in acids, forming *salts of mercury*, or *mercuric salts*. Normal mercuric salts are colourless; the basic salts are frequently yellow. They are partially decomposed by water, with separation of a basic salt, which requires free acid for its solution. The chloride is an exception, being soluble in water without decomposition; hence a solution of chloride of mercury differs in some of its reactions from that of the nitrate and of other salts which are partially decomposed by water. (c) *Hydrosulphuric acid* and *sulphide of ammonium*, when added in very small quantity, give with all mercuric salts a black precipitate of sulphide, Hg^2S, which, when agitated with the mercuric solution, becomes white, owing to the formation of a compound of the sulphide and the undecomposed mercuric salt; further addition of the reagent turns the precipitate brown, and finally black, it being entirely converted into sulphide. This reaction is quite characteristic of mercuric salts. Sulphide of mercury is insoluble in nitric acid, or sulphide of ammonium, soluble in aqua-regia or sulphide of potassium. When sublimed, its colour changes from black to red. *Hydrochloric acid* gives no precipitate with mercuric salts. *Iodide of potassium*, gives a bright red precipitate of iodide, HgI, soluble in excess either of iodide of potassium, or of the mercuric salt. When sublimed its colour changes to a bright yellow. *Cyanide of potassium* gives with nitrate of mercury a white precipitate soluble in excess: it does not precipitate the chloride. *Phosphate of sodium* and *oxalic acid* give white precipitates with mercuric nitrate: with the chloride the precipitate only appears on the addition of ammonia. *Ferrocyanide of potassium* gives with all mercuric salts a white precipitate, which gradually becomes blue, prussian blue being formed, while the filtrate contains cyanide of mercury. *Ferricyanide of potassium* gives no precipitate with the chloride, a yellow precipitate with the nitrate. *Gallic acid* gives an orange-yellow precipitate with all mercuric solutions, except the chloride. *Ammonia* and *carbonate of ammonia* give with all mercuric salts a white precipitate, which is a compound of the mercuric salt with mercuramide: its composition varies according as the ammonia or the mercuric salt is in excess. *Potash* in excess precipitates yellow oxide, Hg^2O, unless the mercuric solution contains much free acid. *Carbonate of potash*, or *potash* in small quantity, precipitates a reddish-brown basic salt. If ammoniacal salts be present, both the fixed alkalis and their carbonates give the white precipitate of mercuramide and mercuric salt. Cyanide of mercury is not decomposed by alkalis; but it is by hydrosulphuric acid. *Carbonate of barium* completely precipitates mercuric nitrate as a basic salt: it gives no precipitate with the chloride. The same reagents which reduce mercurous salts, generally reduce mercuric salts also: but in the case of mercuric salts, the reduction is frequently gradual, a mercurous salt being first formed. Thus *chloride of tin* gives with mercuric salts a white precipitate of subchloride of mercury, which, when boiled with excess of the reagent, is further reduced to metallic mercury. If the solution be poured off, and the reduced mercury boiled with hydrochloric acid, it aggregates into shining globules. *Copper*, *iron*, and *zinc* precipitate metallic mercury from all mercuric solutions which do not contain too much free acid ; the mercury forms a grey deposit on the surface of the metal, which assumes a metallic lustre when rubbed, and disappears when heated. *Protosulphate of iron* reduces mercuric nitrate, but not the chloride. *Formic acid* reduces chloride of mercury to subchloride: no excess of the reagent carries the reduction further, unless the solution be heated nearly to boiling. Mercuric salts are generally decomposed by heat: the chloride and iodide volatilise undecomposed.

Mercurous salts are readily separated from mercuric salts by hydrochloric acid, which precipitates only the former ; and the latter can be detected in the filtrate by various reagents. If much free nitric acid be present, the separation is not complete, for some of the mercurous salt may be converted into mercuric.

Blowpipe reactions.—All mercury compounds, when thoroughly dried, intimately mixed with dry carbonate of sodium, and heated before the blowpipe in a tube closed at one end, are decomposed, and metallic mercury condenses in the cold part of the tube. The mercury compounds which are volatile without decomposition (*e. g.* the chlorides) may escape decomposition by carbonate of soda. In this case, the mixture must be slightly moistened with water, the water expelled by gentle heat over the lamp, and removed with blotting-paper, the tube being held horizontally, to prevent the water from running down to the heated part. When the moisture is all expelled, the blowpipe flame is applied as before. This is an easy and certain method of detecting mercury.

Separation and estimation of Mercury.—The volatility of all its compounds, and the insolubility of its sulphide in strong nitric acid, distinguish mercury from all other metals. Mercury is separated from all the metals of Subdivision A by the insolubility of its sulphide in sulphide of ammonium. In the analysis of a solution, it is better, before treating it with hydrosulphuric acid, to remove by hydrochloric acid those metals which form insoluble chlorides. *Silver* and *subsalts of mercury* are thus entirely, *lead* partially, precipitated. The chloride of lead is removed by boiling the precipitate in a large quantity of water. The chloride of silver and subchloride of mercury are separated by treatment with ammonia, which dissolves the chloride of silver, and blackens the subchloride of mercury; or they may be separated by aqua-regia in the cold, which dissolves the subchloride of mercury, and leaves the chloride of silver undissolved. But, for the complete separation of mercury from *lead* and *silver*, it is better to ensure the presence of mercury only as mercuric salt, by boiling the solution with nitric acid. The silver can then be separated completely by hydrochloric acid. Or the silver may be separated from the mercury by cyanide of potassium, as follows. The solution is nearly neutralised with an alkaline carbonate, and cyanide of potassium added till the precipitate first formed is entirely redissolved: excess of nitric acid is then added, when all the silver is precipitated as cyanide, while cyanide of mercury remains in solution. *Lead* may also be separated from mercury by cyanide of potassium: the addition of nitric acid decomposes the cyanide of lead, forming nitrate, whence the lead may be precipitated by an alkaline carbonate: the cyanide of mercury is not decomposed, and remains in solution. Or the lead may be separated by means of sulphuric acid, which must be in excess, otherwise a basic sulphate of mercury may be precipitated with sulphate of lead. Or the solution may be evaporated to dryness with excess of hydrochloric acid, and the residue treated with alcohol, which dissolves the chloride of mercury, leaving the chloride of lead undissolved.

For the analysis of a mixture of oxide of mercury, cinnabar, and red lead, Wöhler gives the following process. By digestion with dilute nitric acid, the oxide of mercury and protoxide of lead are dissolved; the lead is precipitated from the solution by dilute sulphuric acid, and then the mercury by hydrosulphuric acid or chloride of tin. The residue is then treated on the filter with a mixture of warm dilute nitric and oxalic acids, which dissolves out the binoxide of lead, and the residual cinnabar is washed, dried, and weighed.

Mercury is estimated either in the metallic state; as subchloride, Hg^2Cl; or as sulphide, Hg^2S. In the first case, the solution, which must not contain free nitric acid, is digested with chloride of tin, or phosphorous acid, the reduced mercury washed, dried without the application of heat, and weighed. In the dry way the operation is thus performed. About an inch of carbonate of calcium is introduced into the closed end of a combustion tube, then the mercury compound mixed with quicklime, then about two inches of quicklime. The open end of the tube is bent down and inserted into a narrow-mouthed bottle containing water, the end of the tube just dipping into the water. The layer of quicklime is then heated to redness. then the mercury-compound, and finally the carbonate of calcium, when carbonic anhydride is evolved, and sweeps all the mercury-vapour into the receiver, which must be kept cold. The condensed mercury is then dried and weighed. In the second case, the mercury is best precipitated by an alkaline formate. If the mercury be contained in the solution in any other form than the chloride, hydrochloric acid must be added. the solution nearly neutralised with potash, an alkaline formate added, and the whole digested for some days at a temperature not exceeding 80° : if the solution were boiled, the mercury would be reduced to the metallic state. The subchloride is collected on a weighed filter, dried at a gentle heat, and weighed. Mercury can only be estimated as sulphide in solutions from which hydrosulphuric acid precipitates the sulphide pure, (*e. g.* chloride of mercury): it is then sufficient to collect the sulphide on a filter, dry it in the water-bath, and weigh it. But if the sulphide be precipitated from a solution containing free nitric acid, or a sesquisalt of iron, it is mixed with sulphur, and cannot be weighed directly. In this case, the mercury must be separated from it in the metallic state, either in the wet or dry way, as above described.

In amalgams, the amount of mercury may be determined by the loss of weight produced by heat.

4. **Bismuth.** Bi. Atomic weight, 208.

Found native: also in combination with oxygen, sulphur, tellurium, &c. It is a white metal with a reddish tinge: fuses at 260°. It is not affected by the air at the ordinary temperature: at a white heat it takes fire, forming bismuthic oxide, $Bi^2 O^3$. Hydrochloric acid scarcely attacks it: nitric acid dissolves it readily: sulphuric acid attacks it when hot and concentrated. Powdered bismuth burns in chlorine at the ordinary temperature, forming volatile chloride, $BiCl^3$.

OXIDES OF BISMUTH. *Bismuthic Oxide*, Bi^2O^3. *Bismuthic Anhydride*, Bi^2O^5.

a. *Teroxide of Bismuth. Bismuthic oxide.* Bi^2O^3.—A yellow powder, obtained by heating bismuth in the air, or by gently igniting the nitrate. It grows darker when heated: it may be fused to a glass, which is yellow and crystalline on cooling. It is not volatile. It is insoluble in water, soluble in all acids, forming *bismuthic salts*, which are colourless. They are partially decomposed by *water*, a basic salt being precipitated, and troubling the solution: the addition of free acid dissolves the precipitate. This is the reaction chiefly employed for the detection of bismuth. The decomposition of the chloride by water is more complete than that of any other salt: hence it is well, in searching for small quantities of bismuth, to evaporate the solution to a small bulk with hydrochloric acid in a watch-glass, and add excess of water. The precipitate thus obtained is insoluble in tartaric acid. (Distinction of bismuth from antimony.) *Hydrosulphuric acid* and *sulphide of ammonium* give a black-brown precipitate of sulphide, Bi^2S^3, insoluble in alkaline sulphides, soluble in nitric acid. *Sulphuric acid* gives no precipitate. *Chromate of potassium* precipitates yellow chromate, soluble in nitric acid, insoluble in potash; by which it is distinguished from chromate of lead. *Iodide of potassium* precipitates brown iodide, BiI^3, soluble in excess. *Cyanide of potassium* gives a white precipitate, insoluble in excess, soluble in acids. *Ferrocyanide of potassium* gives a white precipitate; *ferricyanide of potassium*, a pale yellow precipitate, both insoluble in hydrochloric acid. *Alkaline carbonates* precipitate a white basic carbonate, slightly soluble in excess, precipitated from the solution by potash. *Ammonia* and *potash* precipitate white hydrate, insoluble in excess: by boiling it is converted into the yellow oxide. *Zinc*, and several other metals, reduce metallic bismuth from its salts. All bismuth-salts, except the chloride, are decomposed when heated in the air.

b. *Bismuthic Anhydride*, Bi^2O^5.—A light-red powder, obtained by exposing the oxide, suspended in a strong solution of potash, to the action of chlorine. By ignition it is converted into the oxide. Heated with strong sulphuric or nitric acid it evolves oxygen, and forms a bismuth-salt. With hydrochloric acid in the cold it evolves chlorine, and forms chloride of bismuth. It is somewhat soluble in potash, and forms a few double salts of bismuth and potassium.

There are several oxides intermediate between bismuthic oxide and anhydride, which may be regarded as compounds of these two. They are all converted into the oxide by ignition, and evolve chlorine when treated with hydrochloric acid.

Blowpipe reactions.—All bismuth compounds, when heated on charcoal with carbonate of sodium in the inner flame, give a brittle metallic bead, and a yellow incrustation, which disappears when heated in the inner flame, without giving any colour to the outer flame (distinction of bismuth-oxide from lead-oxide). With *borax* and *microcosmic salt* bismuthic oxide gives beads which are yellowish when hot and colourless when cold. If much oxide be employed, the bead is opaque.

Separation and estimation of Bismuth.—The best qualitative test for bismuth is the decomposition of its chloride by water: the precipitate thus produced is insoluble in tartaric acid, potash, and sulphide of ammonium. From the metals of Subdivision A, bismuth is separated by the insolubility of its sulphide in sulphide of ammonium. From *lead*, by means of sulphuric acid in excess: or by evaporation to dryness with hydrochloric acid and treating the residue with alcohol and ether, which dissolves the chloride of bismuth only. From *silver*, by hydrochloric acid. From *mercury*, by the solubility of its sulphide in nitric acid, or by the reduction of the mercury by chloride of tin.

Bismuth is always estimated as oxide. It is best precipitated by carbonate of ammonium, by which it is completely thrown down after some hours standing in a warm place. The precipitate is converted into oxide, Bi^2O^3, by ignition in a porcelain (not a platinum) crucible. Bismuth cannot be precipitated directly by carbonate of ammonium from a solution containing hydrochloric acid, for the precipitate would contain some oxychloride: in this case it must be precipitated as sulphide, the sulphide dissolved in nitric acid, and the solution precipitated by carbonate of ammonium.

5. **Copper.** Cu. Atomic weight, 31·7.

Found native: as suboxide (red copper-ore): as basic carbonate (malachite), sulphate, phosphate, &c.: as sulphide (copper-glance): as sulphide of copper and other metals (copper-pyrites, bournonite, fahl-ore, &c.). It has a red colour and a strong metallic lustre: it is very ductile and tenacious, and difficultly fusible. It is not affected by dry air at the ordinary temperature: in moist air it becomes covered with a green coating of carbonate: in presence of acids it is rapidly oxidised by the air. When heated in the air it is converted into black oxide. Hydrochloric acid dissolves it but slightly, forming subchloride, Cu^2Cl: nitric acid dissolves it readily: concentrated sulphuric acid dissolves it on heating, forming sulphate, SO^4Cu^2. Heated in chlorine it forms a mixture of chloride, CuCl, and subchloride.

OXIDES OF COPPER. *Suboxide*, Cu^4O. *Oxide*, Cu^2O.

a. *Suboxide of Copper. Cuprous Oxide.* Cu^4O.—A red powder, obtained by heating the oxide with metallic copper, or by boiling a protosalt of copper with grape-sugar, arsenious acid, &c., in presence of excess of potash. When heated in the air it is converted into oxide. All acids, except hydrochloric, decompose it into metallic copper, and cupric oxide, which dissolves in the acid, forming a protosalt. Hydrochloric acid dissolves it without decomposition, forming a solution of subchloride, Cu^2Cl, which is colourless when pure, but rapidly becomes brown, and then green, by absorption of oxygen and formation of chloride (p. 6). From the acid solution of subchloride, *water* precipitates white subchloride. *Potash* precipitates yellow subhydrate, insoluble in excess, which rapidly becomes black by absorption of oxygen and conversion into oxide. *Ammonia* in excess gives a colourless solution, which rapidly becomes blue on exposure to the air. In short, all subsalts of copper absorb oxygen very readily from the air, and are converted into protosalts.

b. *Oxide of Copper. Cupric Oxide.* Cu^2O.—A black powder, obtained by heating copper in the air, or by igniting the nitrate. It fuses at a high temperature. At a red heat it readily parts with its oxygen to hydrogen or carbon, which renders it a valuable agent in organic analysis. It is insoluble in water; soluble in acids, forming *protosalts of copper*, or *cupric salts.* These are mostly colourless when anhydrous: when hydrated they are blue or green. An aqueous solution of a normal copper-salt reddens litmus-paper. *Hydrosulphuric acid* or *sulphide of ammonium* gives with cupric salts a black precipitate of sulphide, Cu^2S, which is rapidly oxidised into sulphate by exposure to the air: it is insoluble in hydrochloric acid or sulphide of potassium; slightly soluble in sulphide of ammonium; soluble in nitric acid or cyanide of potassium. *Iodide of potassium*, in presence of sulphurous acid or a protosalt of iron, precipitates all the copper as greenish-white subiodide, Cu^2I, soluble in excess. *Cyanide of potassium* gives a greenish-yellow precipitate of cyanide, CNCu, soluble in excess: from this solution hydrochloric acid precipitates white subcyanide, $CNCu^2$, soluble in excess: hydrosulphuric acid gives no precipitate. (C) *Ferrocyanide of potassium* gives a red-brown precipitate of cyanide of iron and copper, insoluble in hydrochloric acid, soluble in ammonia, decomposed by potash with separation of hydrate of copper. In very dilute solutions only a brown colour is produced. This is the most delicate test for copper. *Ferricyanide of potassium* gives a yellowish-green precipitate, insoluble in hydrochloric acid. *Fixed alkaline carbonates* give (with evolution of carbonic anhydride) a greenish-blue precipitate of basic carbonate, which on boiling is converted into black oxide. *Fixed alkalis* in excess precipitate blue hydrate, CuHO, insoluble in excess, which on boiling is converted into black oxide. The presence of many organic substances prevents this precipitation. For instance, if grape-sugar be present in a solution of sulphate of copper, potash or soda produces a deep blue solution, whence the whole of the copper is precipitated on boiling as suboxide. (c) *Ammonia* or *carbonate of ammonium* in small quantity precipitates a greenish-blue basic salt, readily soluble in excess to a beautiful dark-blue solution, whence black oxide may be separated by boiling with potash. The blue colour is perceptible in very dilute copper solutions. Metallic *zinc* and *iron* precipitate copper from its solutions in presence of free hydrochloric acid. All soluble copper-salts are decomposed by ignition in the air.

Blowpipe reactions.—All copper compounds are reduced when heated on charcoal in the inner flame with carbonate of sodium and cyanide of potassium, yielding red metallic scales, which are easily detected by levigating the fused mass in an agate mortar. Both oxides of copper, and most copper-salts, when heated on a platinum-wire in the inner flame, give an intense green colour to the outer flame (especially on addition of a little chloride of silver). With *borax* and *microscomic salt*, copper-salts give in the outer flame clear beads, which are dark-green when hot, bluish-green when cool: in the inner flame (especially on addition of tin) beads which are colourless when hot, red, and frequently opaque, when cool.

Separation and estimation of Copper.—Copper is separated from the metals of Subdivision A, by the insolubility of its sulphide in sulphide of potassium or sodium. From *lead* it is separated by sulphuric acid, or by cyanide of potassium in excess, which precipitates the lead only. From *silver*, it is separated by hydrochloric acid. From *mercury*, by adding excess of cyanide of potassium, and passing hydrosulphuric acid through the solution, when sulphide of mercury is precipitated alone. From *bismuth*, by carbonate of ammonium, or cyanide of potassium.

When copper is precipitated as sulphide, the sulphide must be washed with water containing hydrosulphuric acid, to prevent oxidation from the air and the consequent passage of soluble sulphate through the filter: the sulphide is then dissolved in nitric acid, and the solution precipitated by potash. Copper cannot be accurately estimated by precipitation by iron in the metallic state: since the reduced copper becomes partially oxidised during the process of drying.—Rose.

6. **Cadmium.** Cd. Atomic weight, 56.

Found principally in zinc-ores. It is a white metal, much resembling tin: it is nearly as volatile as mercury. It is not affected by dry air at the ordinary temperature: in moist air it is slightly oxidised: heated in the air it burns, and forms brown vapours of oxide of cadmium. It is soluble in hydrochloric, sulphuric, and even acetic acids: most easily in nitric acid.

Oxide of Cadmium. *Cadmic Oxide,* Cd^2O.—A brown powder, obtained by heating cadmium or the hydrate in the air. It is not fused or decomposed by the strongest heat. It is soluble in acids, forming *salts of cadmium,* or *cadmic salts.* These are colourless, mostly soluble in water: the aqueous solution of the normal salts reddens litmus-paper. (c) *Hydrosulphuric acid* or *sulphide of ammonium* gives, even in very acid solutions, a yellow precipitate of sulphide, Cd^2S, insoluble in alkaline sulphides, caustic alkalis, or cyanide of potassium, soluble in nitric acid. *Alkaline phosphates* and *oxalates* give white precipitates, insoluble in water, soluble in ammonia. *Cyanide of potassium* precipitates white *cyanide of cadmium,* CNCd, soluble in excess: from this solution hydrosulphuric acid precipitates the sulphide. *Ferrocyanide of potassium* gives a white precipitate; *ferricyanide of potassium* a yellow precipitate; both soluble in hydrochloric acid. *Alkaline carbonates* precipitate white carbonate, CO^3Cd^2, insoluble in excess. *Potash* precipitates white hydrate, CdHO, insoluble in excess. *Ammonia* precipitates the hydrate, soluble in excess: this solution is precipitated by hydrosulphuric acid. Metallic *zinc* precipitates cadmium from its solutions.

Blowpipe reactions.—All cadmium compounds, when heated on charcoal in the inner flame with carbonate of sodium and cyanide of potassium, give a brown incrustation of cadmic oxide. A little cadmic oxide in presence of excess of zinc-oxide may be detected by heating the mixture with carbonate of sodium for an instant in the inner flame, when a slight incrustation of cadmic oxide is formed. Much longer heat is required for the formation of zinc-oxide. With *borax* and *microcosmic salt* cadmic oxide gives a bead, which is yellowish when hot, and colourless when cool.

Separation and estimation of Cadmium.—For the detection of cadmium in zinc-ores, the mineral is powdered, and digested in aqua-regia, the solution diluted with water, and saturated with hydrosulphuric acid, which does not precipitate the zinc. The precipitate, which generally contains some sulphide of copper, is washed with water containing hydrosulphuric acid, dissolved in nitric acid, the solution precipitated by excess of carbonate of ammonium and the whole digested for some time at a gentle heat. The precipitate (in the absence of lead and bismuth) consists entirely of carbonate of cadmium: the filtrate contains all the copper.

Cadmium is separated from the metals of Subdivision A, by the insolubility of its sulphide in alkaline sulphides. From *lead* it is separated by sulphuric acid, or by cyanide of potassium: from *silver*, by hydrochloric acid. From *mercury*, it is separated by reducing the mercury by chloride of tin: or by excess of cyanide of potassium and nitric acid, as described in the separation of mercury from lead (p. 126). From *bismuth*, by ammonia, or by cyanide of potassium. From *copper*, by carbonate of ammonium, which dissolves the copper, but precipitates the cadmium. Or by cyanide of potassium, as follows:—cyanide of potassium is added to the solution till the precipitate first formed is redissolved (or, if the solution be ammoniacal, till the blue colour is destroyed); the solution is then saturated with hydrosulphuric acid, which precipitates only sulphide of cadmium. The filtrate is heated to expel excess of hydrosulphuric acid, more cyanide of potassium added, the whole heated with hydrochloric acid with addition of nitric acid until all the hydrocyanic acid is expelled, and the copper precipitated from the solution by potash.

Cadmium is always estimated as oxide. It is precipitated by carbonate of sodium as carbonate, which by ignition is converted into oxide.

7. **Palladium.** Pd. Atomic weight, 53.

Found native in platinum-ores, and in gold-dust from Brazil. It closely resembles platinum in appearance, but is not nearly so heavy. It is insoluble in hydrochloric acid: somewhat soluble in boiling concentrated sulphuric acid: slowly but completely soluble in nitric acid (which distinguishes it from platinum): readily soluble in aqua-regia, the solution containing a mixture of nitrate and chloride of palladium.

Oxides of Palladium.—The most important oxide is

Protoxide of Palladium. Palladous Oxide. Pd^2O.—A black powder, obtained by dissolving palladium in nitric acid, evaporating the dark-brown solution to dryness, and igniting the nitrate at a gentle heat. The hydrate, $PdHO$, is dark-brown: it is obtained by precipitating a palladium-salt by carbonate of potassium: at a moderate heat it is converted into the oxide, at a stronger heat it is reduced to the metal. *Hydrosulphuric acid* or *sulphide of ammonium* gives with salts of palladium a dark-brown precipitate of sulphide, Pd^2S, soluble in strong acids, insoluble in alkaline sulphides. *Hydriodic acid* and soluble *iodides* give even in very dilute solutions a black precipitate of iodide, PdI, somewhat soluble in excess of iodide of potassium. This reaction serves for the estimation of iodine in mineral springs. *Cyanide of mercury* gives (sometimes not immediately) a yellowish gelatinous precipitate of cyanide, $CNPd$, which becomes white on standing: it is soluble in cyanide of potassium, ammonia, and in a large quantity of hydrochloric acid. *Carbonate of potassium* precipitates brown hydrate, $PdHO$, soluble in excess, reprecipitated by boiling the solution. *Potash* precipitates a yellowish-brown basic salt, soluble in excess. *Ammonia* and *carbonate of ammonium* do not precipitate nitrate of palladium, but if added in excess, they decolorise the solution. With chloride of palladium they give a reddish-yellow precipitate of chloride of palladammonium, NH^3PdCl, soluble in excess, and reprecipitated by hydrochloric acid. *Chloride of ammonium* does not precipitate palladium-salts. *Chloride of tin* gives a black precipitate, which dissolves in hydrochloric acid with an intense green colour. Palladium-salts are reduced by *phosphorous*, *sulphurous*, *nitrous*, and *formic* acids, metallic *zinc* and *iron*, and by *alcohol*. *Protosulphate of iron* reduces the nitrate, but not the chloride. All palladium-salts are decomposed by ignition, leaving metallic palladium.

Separation and estimation of Palladium.—Palladium is separated from most other metals by cyanide of mercury. If, however, the solution contain alcohol, gold, platinum, and some other metals would also be precipitated by cyanide of mercury. Palladium cannot be separated from platinum by nitric acid, for an alloy of palladium with very little platinum is completely dissolved by nitric acid. They may be separated by fusion with acid sulphate of potassium, when the platinum is not oxidised, while the palladium is converted into sulphate. An effectual qualitative reaction for distinguishing palladium-foil from platinum-foil is to moisten it with a drop of an alcoholic solution of iodine, which is then left to spontaneous evaporation; when on palladium-foil a black stain is produced, which disappears on heating, while platinum-foil remains unaltered.

Palladium cannot be separated from *copper* (which often occurs in platinum ores) by cyanide of mercury. Berzelius gives the following process. The two metals are precipitated as sulphides, and the precipitate, while still moist, roasted together with the filter, as long as sulphurous anhydride continues to be evolved. They are thus converted into basic sulphates, which are dissolved in hydrochloric acid, chloride of potassium added, and the whole evaporated to dryness. A dark residue is left, consisting of chloride of potassium, chloride of copper and potassium, and chloride of palladium and potassium; the two former salts are dissolved out by alcohol of sp. gr. 0·833, the residue dried, weighed, and the amount of palladium calculated from it. According to Döbereiner, copper may be separated from palladium by reducing the latter metal by an alkaline formate.

Palladium is always estimated in the metallic state. It is precipitated by cyanide of mercury (the solution having been nearly neutralised by carbonate of sodium): the cyanide on ignition leaves metallic palladium.

8. **Rhodium.** R. Atomic weight, 52.

Found in small quantity in platinum-ores. It is a grey powder, which can only be imperfectly fused to a coherent mass. It is oxidised when strongly heated in the air. When pure it is insoluble in acids: when alloyed with other metals it may be partially dissolved. It is dissolved when fused with acid sulphate of potassium or glacial phosphoric acid. It is oxidised when ignited with potash and nitrate of potassium. When rhodium is mixed with powdered chloride of potassium, and heated to redness in a stream of chlorine, a double chloride of rhodium and potassium is formed, which is soluble in water.

OXIDES OF RHODIUM.—The most important oxide is

Sesquioxide of Rhodium. Rhodic Oxide. R^4O^3.—A black powder, insoluble in acids, obtained by the prolonged ignition of the hydrate. The hydrate is obtained by fusing rhodium with potash and nitrate of potassium, washing with water the compound of rhodic oxide and potash which is thus formed, and digesting it in hydrochloric acid, when the hydrate remains of a greyish-green colour, insoluble in acids. The hydrate obtained by precipitating the double chloride of rhodium and potassium by an alkali, and evaporating to dryness, is slowly soluble in acids, together with the alkali which adheres to it, forming double salts. Rhodium-salts are difficult to obtain, owing to the insolubility of the metal and its oxide in acids: they are best prepared in the dry way by one of the methods described above. Their solutions are generally red. They are slowly precipitated by *hydrosulphuric acid* or *sulphide of ammonium*, as brown sulphide, insoluble in alkaline sulphides. *Chloride of tin* gives no precipitate, but colours the solution dark-brown. *Nitrate of silver* gives with chloride of rhodium a red precipitate, analogous in composition to the iridium precipitate (p. 104). *Potash* gives with chloride of rhodium a yellowish-brown precipitate of hydrate, soluble in excess: in other rhodium-salts this precipitate only appears on boiling. *Ammonia* gives with all rhodium-salts a yellow precipitate containing rhodic oxide and ammonia, soluble in hydrochloric acid. Rhodium-salts are reduced by metallic *zinc:* not by *protosulphate of iron.* (c) From a solution of a rhodium-salt, saturated with potash, *alcohol* reduces metallic rhodium, even in the cold, as a black powder: with other platinum-metals*, this reaction only takes place on heating.

Separation and estimation of Rhodium.—Rhodium may be separated from all the noble metals (except *palladium* and *silver*) by its solubility when fused with acid sulphate of potassium. The insolubility in alcohol of chlororhodate of sodium affords a method of separating it from other platinum-metals.—Rose.

For further details as to the separation of rhodium from the platinum-metals, see the article on platinum-ores in Part IV. p. 237. For the separation of rhodium from *copper*, Berzelius gives the following method:—The solution is saturated with hydrosulphuric acid and left in a stoppered bottle for twelve hours in a warm place: the sulphides are then filtered off, and the filtrate heated, on which more sulphide of rhodium generally separates. The sulphides are then roasted in a platinum crucible till they are completely oxidised: they are then treated with hydrochloric acid, which dissolves out the copper and leaves the rhodic oxide. The filtrate from the sulphides still contains some rhodium, which is separated as rhodic oxide by evaporating to dryness with carbonate of sodium, and treating the residue, after ignition, with cold water. The rhodic acid is then reduced by hydrogen at a gentle heat and weighed.

Rhodium is always estimated in the metallic state. The rhodic oxide is obtained by evaporation with carbonate of sodium as above, and reduced by hydrogen.

9. **Ruthenium.** Ru. Atomic weight, 52.

Found in small quantity in platinum-ores. It is a grey metal, closely resembling iridium. When heated in the air it becomes covered with black sesquioxide, Ru^4O^3. When pure it is insoluble in acids, or in fused acid sulphate of potassium. When heated with potash and nitrate of potassium, it is oxidised and converted into ruthenate of potassium, a dark-green mass which is soluble in water, forming a yellow solution, from which nitric acid precipitates a black hydrate.

OXIDES OF RUTHENIUM. The most important oxide is

Sesquioxide of Ruthenium, Ru^4O^3.—A black powder insoluble in acids, obtained by heating ruthenium in the air. It does not lose its oxygen at a white heat. The hydrate precipitated by nitric acid from ruthenate of potassium is soluble in hydrochloric acid, forming a dark brown solution of sesquichloride of ruthenium, which gives the following reactions:—It is decomposed by *heat* into black sesquioxide and hydrochloric acid. (c) *Hydrosulphuric acid* slowly precipitates brown sulphide of ruthenium; while the solution is coloured blue, owing to the reduction of the sesquichloride to protochloride. This is a very delicate and characteristic reaction. *Sulphide of ammonium* precipitates brown sulphide, slightly soluble in excess, forming a yellow solution. *Cyanide of mercury* gives a blue precipitate and colours the solution blue. *Sulphocyanate of potassium* gives (when other platinum-metals are absent) a purple-red precipitate, which becomes violet on heating. *Acetate of lead* gives a purple-red precipitate. (c) *Nitrate of silver* gives a black precipitate, which is a mixture of chloride of silver and sesquihydrate of ruthenium: the latter gradually dissolves in the free nitric acid, leaving white chloride of silver: the addition of ammonia dissolves the chloride of silver and reprecipitates the sesquihydrate. *Caustic alkalis*, *alkaline carbonates*, *and phosphate of sodium*, precipitate black hydrate, insoluble in excess. Metallic *zinc* first gives a blue colour to the solution, and then gradually precipitates metallic ruthenium, while the solution becomes colourless. *Sulphurous*, *oxalic*, *and formic acids* decolorise the solution, but do not reduce the metal. The *chlorides of potassium* and *ammonium* precipitate crystalline violet double chlorides, difficultly soluble in water, insoluble in alcohol. The solution of the double chloride of ruthenium and potassium is decomposed by heat, with separation of a black oxychloride.

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* By this term are meant those metals which are usually found accompanying platinum in its ores.

Separation and estimation of Ruthenium.—Ruthenium has hitherto been found associated only with the platinum-metals, from which it is separated as described in Part IV. (p. 239).

Ruthenium is always estimated in the metallic state. It is precipitated as sesquihydrate from a solution of sesquichloride, either by simple heat or by an alkali; and from ruthenate of potassium by nitric acid. The sesquihydrate generally contains some alkali, which cannot be removed by washing. It must be reduced by gentle ignition in a stream of hydrogen, the reduced mass thoroughly washed with water, and the residual ruthenium, before weighing, again ignited and left to cool in a stream of hydrogen, as it would be partially oxidised if allowed to cool in the air.

10. **Osmium.** Os. Atomic weight, 100.

Found in platinum-ores, chiefly as osmide of iridium. It is generally obtained as a grey porous metallic mass. It combines with oxygen more readily than any other platinum-metal. When heated in contact with the air it is entirely converted into osmic anhydride, OsO^2. It is slowly soluble in ordinary nitric acid, more readily in aqua-regia, or fuming nitric acid: the solution in all cases contains osmic acid. After strong ignition, out of contact with air, osmium is insoluble in acids. Heated in chlorine, it is converted into a mixture of green chloride and red bichloride ($OsCl$ and $OsCl^2$), of which the latter is the more volatile.

Oxides of Osmium.—Osmium forms several compounds with oxygen, of which the most important are the *Binoxide*, Os^2O^2, and *Osmic Anhydride*, OsO^2.

a. *Binoxide of Osmium. Osmic Oxide.* Os^2O^2.—A black powder, obtained by igniting the hydrate in an atmosphere of carbonic anhydride. The hydrate is precipitated (black) when an aqueous solution of chlorosmate of potassium is boiled with carbonate of sodium. The chlorosmate of potassium, $OsCl^3K$, is obtained by heating a mixture of metallic osmium and chloride of potassium in a stream of chlorine. It is a red compound, insoluble in alcohol, somewhat soluble in water, forming a yellow solution, which gives the following reactions. *Hydrosulphuric acid* and *sulphide of* *ammonium* precipitate slowly yellowish-brown sulphide, insoluble in alkaline sulphides. *Tannic acid*, on heating, gives a blue colour, and no precipitate: *ferrocyanide of potassium*, first a green, then a blue, colour: *iodide of potassium*, a deep purple-red colour, which does not disappear on heating: *chloride of tin*, a brown precipitate: *nitrate of silver*, a dark olive-green precipitate, which contains the whole of the osmium. *Oxalic acid* and *protosulphate of iron* give no reaction. *Potash* gives a black, *ammonia* a brown, precipitate, slowly in the cold, immediately on boiling. Metallic *zinc* and *formate of sodium* reduce metallic osmium.

b. *Osmic Anhydride*, OsO^2. A white crystalline mass, obtained by heating osmium or any of its lower oxides, in contact with the air. It is volatile, and may be sublimed in needles, evolving vapours of a characteristic and disagreeable smell, which irritate the eyes violently. It is somewhat soluble in water: the solution contains *osmic acid*, and reddens litmus very feebly, if at all. The addition of potash gives a yellow solution of *osmate of potassium*, in which a few drops of alcohol give a rose-red precipitate of *osmite of potassium*. This lower oxygen-acid of osmium (osmous acid) is only known in combination with two or three bases. The addition of a mineral acid to a solution of osmate of potassium sets free osmic acid, which may be recognised by its peculiar smell, and which may be isolated by distillation. Metallic osmium is reduced from an aqueous solution of osmic acid by *sulphurous acid*, *protosulphate of iron*, or metallic *zinc*. *Chloride of tin* gives a brown precipitate, soluble in hydrochloric acid to a brown solution. *Hydrosulphuric acid* or *sulphide of ammonium* precipitate black-brown sulphide.

Separation and estimation of Osmium.—The best method of separating osmium from the other platinum-metals (especially iridium) is to volatilise it in the form of osmic anhydride, either by distillation with aqua-regia (if the compound be soluble therein), or by roasting in a stream of oxygen. The acid vapours are collected in a strong solution of potash, whence a few drops of alcohol precipitates all the osmium as osmite of potassium. The precipitate is digested with chloride of ammonium, and the double chloride thus formed reduced to metallic osmium by ignition in a stream of hydrogen. (Frémy.) The separation of osmium in the native osmide of iridium is a difficult matter: for the osmium cannot be completely dissolved out by acids, nor converted into osmic acid by heating in oxygen, nor into chloride by heating in chlorine. The best way to decompose this compound is to oxidise it by fusion with nitrate of potassium, or a mixture of caustic potash and chlorate of potassium.—(Fritzsche and Struve. J. Pr. Ch. xxxvii. 483.)

Osmium is generally estimated in the metallic state.

GROUP II.

Metals which are not precipitated by hydrosulphuric acid, but which are completely precipitated by sulphide of ammonium, from acid solutions.

This group like the former, comprises two subdivisions:—

A.—Metals which are precipitated as sulphides: *nickel, cobalt, manganese, zinc, iron, uranium.*

B. — Metals which are precipitated as hydrates: *aluminium, beryllium* or *glucinum, zirconium, thorium, yttrium, erbium, terbium, cerium, lanthanum, didymium: titanium, tantalum, niobium, chromium.* The first ten metals in this subdivision are known as *the metals of the earths*, or *earthy metals.*

Group II.—Subdivision A.

The sulphides of these metals are insoluble in water, but more or less soluble in dilute mineral acids: hence they are not precipitated by hydrosulphuric acid from a solution containing sufficient free mineral acid. From a neutral solution their precipitation by hydrosulphuric acid is not complete: for the acid with which the precipitated metal was combined, is set free, and (if a mineral acid) holds, at least, a portion of the sulphides in solution. From an alkaline solution they are completely precipitated by hydrosulphuric acid. By sulphide of ammonium they are completely precipitated, either from an acid or a neutral solution, the free acid being neutralised by the alkali contained in the alkaline sulphide.

The metals of this division are all soluble in dilute mineral acids, generally with evolution of hydrogen: their sulphides, when treated with dilute mineral acids, evolve hydrosulphuric acid. The sulphides of nickel and cobalt are decomposed with difficulty by acetic or dilute hydrochloric acid: sulphide of zinc is insoluble, sulphide of manganese readily soluble, in acetic acid. All these metals (except zinc) form sesquisalts, as well as protosalts: the sesquisalts of manganese, cobalt, and nickel, are less stable than those of iron and uranium, being reduced to protosalts on boiling their solutions. The protosalts are not precipitated by ammonia in presence of chloride of ammonium, a double salt of the metal and ammonium being formed, which is not decomposed by ammonia. The sesquisalts of these metals are completely precipitated by ammonia in presence of chloride of ammonium. The presence of tartaric acid, and of many other non-volatile organic compounds, hinders the precipitation of the sesquisalts by caustic alkalis, or alkaline carbonates; but not that by sulphide of ammonium. When in the form of double cyanides, these metals are not precipitated by sulphide of ammonium (p. 39). The sesquisalts are precipitated from their neutral solutions by digestion with *carbonate of barium* or of *calcium*, in the cold; by *benzoate* or *succinate of ammonium;* or by heating with *acetate of sodium.* The protosalts are not precipitated under similar circumstances.

1. **Nickel.** Ni. Atomic weight, 29.

Found as arsenide (copper-nickel) and arsenate (nickel-ochre); as sulphide, both alone and combined with other metallic sulphides: in very small quantities, and generally accompanied by cobalt, in meteoric iron, olivine, manganese-ore, &c. It is a white metal, hard, malleable, and magnetic. It is not oxidised by the air at the ordinary temperature: heated in the air it is slowly and imperfectly converted into the oxide, Ni^2O. When finely powdered, and heated in chlorine, it takes fire, and is converted into chloride, NiCl.

OXIDES OF NICKEL. *Protoxide*, Ni^2O. *Sesquioxide*, Ni^4O^3.

a. *Protoxide of Nickel*, Ni^2O. — A black powder, obtained by igniting the hydrate, nitrate, or carbonate of nickel. It is soluble in acids, forming *nickel-salts*, which are green when in solution or when they contain water of crystallisation, yellow when perfectly anhydrous. Their solution reddens litmus. *Hydrosulphuric acid* does not precipitate nickel-salts at all from an acid solution; only very partially from a neutral solution of a salt of a mineral acid: *acetate of nickel*, or any nickel-salt mixed with acetate of sodium, it precipitates entirely on heating the solution, unless a large excess of free acetic acid be present. The precipitated sulphide, Ni^2S, is black, difficultly soluble in dilute hydrochloric or acetic acid, readily soluble in nitric acid, or aqua-regia. *Sulphide of ammonium* precipitates sulphide of nickel, slightly soluble in the reagent, forming a dark-brown solution, whence the sulphide is precipitated by boiling. (Hence, if the filtrate from the sulphide of ammonium precipitate has a brown colour, it is a sign of the probable presence of nickel.) *Hydrocyanic acid* precipitates all the nickel as greenish-white cyanide, $CNNi$, from acetate of nickel, or from any nickel-salt mixed with sufficient acetate of sodium. *Cyanide of potassium* precipitates the cyanide from all nickel-salts: excess of the reagent dissolves the cyanide of nickel, forming a soluble double cyanide of nickel and potassium, which is decomposed by dilute sulphuric or hydrochloric acid, hydrocyanic acid being evolved, and cyanide of nickel precipitated, which requires boiling with excess of acid for its conversion into a soluble nickel-salt. *Ferrocyanide of potassium* gives a greenish white precipitate, *ferricyanide* a yellowish-green precipitate, both insoluble in hydrochloric acid. *Phosphate* or *arsenate of sodium* gives a greenish-white precipitate of phosphate or arsenate of nickel. *Oxalic acid* gradually precipitates all the nickel as greenish-white oxalate, soluble in ammonia: when this solution is exposed to the air, the oxalate of nickel slowly separates out. *Alkaline carbonates* precipitate an apple-green basic carbonate, soluble in excess of carbonate of ammonium to a greenish-blue solution. *Potash* precipitates apple-green hydrate, $NiHO$, insoluble in excess, soluble in ammoniacal salts. *Ammonia* does not precipitate nickel-salts when free acid or chloride of ammonium is present: from neutral solutions it partially precipitates the hydrate, which is soluble in excess, forming a blue solution, whence the hydrate is precipitated on the addition of sufficient potash. If but little nickel be present, the ammoniacal solution becomes distinctly blue only after long exposure to the air. All soluble nickel-salts are decomposed by heat, and are then not entirely soluble in water.

b. *Sesquioxide of Nickel*, Ni^4O^3. — The hydrate is obtained when chlorine is passed through water in which hydrate of nickel is suspended, or through a solution of a nickel-salt mixed with carbonate of barium, or through a solution of cyanide of nickel in presence of free alkali. Excess of dilute hydrochloric acid hinders its formation, decomposing it into chloride of nickel and free chlorine. (On this reaction depends a process for the separation of nickel from cobalt.) It is a very unstable compound: being decomposed by heat into protoxide and free oxygen ; and by acids into a protosalt of nickel, and chlorine (by hydrochloric acid) or oxygen (by other acids).

Blowpipe reactions.—All nickel-salts, when heated with carbonate of sodium on charcoal in the inner flame, are easily reduced to a grey metallic powder, which is attracted by the magnet. With *borax* they give, in the outer flame, a clear bead, which is hyacinth-red when hot, and pale- or dark-yellow (according to the quantity of nickel present) on cooling: the addition of nitrate or any other salt of potassium gives a blue or dark-purple colour to the bead. In the inner flame the bead becomes grey and opaque, owing to the rednction of the metal. With *microcosmic salt* they give in both flames a clear bead which is dark-yellow when hot, and almost colourless when cool.

Separation and estimation of Nickel.—For the analysis of arsenide of nickel (natural or artificial) or of other ores which contain nickel and cobalt with other metals, the finely powdered compound is fused with 6 times its weight of a mixture of equal portions of nitre and carbonate of sodium, the alkaline arsenate thus formed extracted by water, and the remaining oxides dissolved in hydrochloric acid. Or the compound may be fused with three times its weight of sulphur and carbonate of potassium, the alkaline sulpharsenate formed extracted with water, and the residual sulphides dissolved in hydrochloric acid with gradual addition of nitric acid. The acid solution in either case is then nearly neutralised with carbonate of sodium, acetate of sodium added, and the whole heated to boiling, when all the iron is precipitated. The filtrate is acidulated with hydrochloric acid, saturated with hydrosulphuric acid (to remove copper, bismuth, &c.), and filtered: the filtrate heated to expel hydrosulphuric acid, and the cobalt and nickel precipitated by carbonate of sodium, and separated by one of the methods hereafter described. Or the compound is dissolved in concentrated hydrochloric acid, with gradual addition of nitric acid, heated to boiling, nearly neutralised with carbonate of sodium, with addition of acetate of sodium, and (unless the precipitate formed has a reddish-brown colour) of sesquichloride of iron also, the whole boiled for a time, and then filtered from the basic arsenate of iron: the filtrate, which is free from arsenic and iron, is then treated as before. To obtain pure metallic nickel, the solution containing nickel, cobalt (and iron), is treated with acid oxalate of potassium, which precipitates the oxalates of nickel and cobalt: these are thoroughly washed, dissolved in ammonia, and the solution allowed to evaporate spontaneously, when the oxalate of nickel separates out first, while the cobalt-salt remains dissolved, forming a red solution. On igniting the oxalate of nickel pure metallic nickel is obtained. This reaction serves to detect very small traces of cobalt in presence of nickel, but it will not effect an accurate quantitative separation of the two metals.

Nickel is separated from all the metals of Group I. by the non-precipitation of its sulphide from an acid solution.

Nickel is estimated as protoxide. Potash completely precipitates nickel from its salts as hydrate (if the solution be heated): and the hydrate, when washed with hot water, dried, and ignited, is converted into protoxide.

2. **Cobalt.** Co. Atomic weight, 30.

Occurs as sulphate: as arsenate: as arsenide: as sulpharsenide (cobalt-glance): and generally, in small quantity, in nickel- and iron-ores. It is a grey metal; somewhat malleable and magnetic. It is not oxidised by the air, except at a high temperature. Heated in chlorine, it takes fire, and is converted into blue crystalline scales of chloride, CoCl.

Oxides of Cobalt. *Protoxide*, Co^2O. *Sesquioxide*, Co^4O^3. Cobalt also forms other intermediate oxides.

a. *Protoxide of Cobalt*, Co^2O.—An olive-green powder, obtained by gently igniting the hydrate or carbonate out of contact with the air. The hydrate is of a rose-red colour. Both the oxide and hydrate are readily soluble in acids, forming *cobalt-salts*, which are red when in solution, or when they contain water of crystallisation, blue when anhydrous, or when in solution in concentrated free acid. With *hydrosulphuric acid* and *sulphide of ammonium*, cobalt-salts behave precisely like nickel-salts: the black sulphide, Co^2S, is insoluble in sulphide of ammonium: when once formed it is very difficultly soluble in dilute hydrochloric or sulphuric acid, or in acetic acid. (Hence if a black residue remains undissolved when the sulphide of ammonium precipitate is treated with hydrochloric acid, it is probably sulphide of cobalt). A solution of a cobalt-salt mixed with acetate of sodium is completely precipitated by hydrosulphuric acid on heating, more easily than a nickel-salt in similar circumstances. (Separation of cobalt and nickel from manganese.) When *nitrite of potassium* is added to a solution of a cobalt-salt acidulated with acetic or dilute nitric acid, the whole of the cobalt is precipitated as a yellow crystalline compound, which is decomposed by hot nitric or hydrochloric acid, or by potash, very difficultly soluble in water, insoluble in potassium-salts, and strong alcohol: hence the precipitate is best washed first with acetate of potassium, then with alcohol. This reaction is said by Stromeyer to serve for the separation of cobalt from nickel. *Cyanide of potassium* gives with all cobalt-salts (or hydrocyanic acid with acetate of cobalt) a reddish-brown precipitate of cyanide, CNCo, soluble in excess of cyanide of potassium, in ammonia, or chloride of ammonium, insoluble in water or dilute acids. If the cobalt solution contains free acid, (so that hydrocyanic acid is set free on the addition of cyanide of potassium,) and if the solution of cyanide of cobalt in excess of cyanide of potassium be heated for a time, the addition of dilute sulphuric or hydrochloric acid produces no precipitate, all the cobalt being converted into sesquicyanide of cobalt and potassium (cobalticyanide of potassium), $Cy^6Co^2K^3$, which is not decomposed by dilute acids. If the cobalt solution contain any nickel, the addition of hydrochloric acid to the solution of cyanide in cyanide of potassium produces a greenish precipitate, which always contains all the nickel, but only all the cobalt when at least 3 atoms of nickel are present for every 2 atoms of cobalt: in which case the precipitate consists of pure sesquicyanide of cobalt and nickel, $Cy^6Co^2Ni^3$. If a larger proportion of nickel be present, the precipitate contains also cyanide of nickel, which by prolonged boiling in hydrochloric acid is decomposed into hydrocyanic acid and soluble chloride of nickel. If, on the other hand, a larger proportion of cobalt be present, the precipitate consists of sesquicyanide of cobalt and nickel, and some cobalt remains in solution as sesquicyanide of cobalt and potassium. The precipitate of sesquicyanide of cobalt and nickel (when all the cyanide of potassium and cyanide of nickel present have been decomposed by boiling in hydrochloric acid) is decomposed by caustic potash into hydrate of nickel which is precipitated, and sesquicyanide of cobalt and potassium which remains in solution. This reaction is applied as follows for the detection of nickel in presence of cobalt. The solution (which must not contain iron or manganese) is slightly acidulated with hydrochloric acid, excess of cyanide of potassium added, and the whole heated to boiling: if a precipitate is produced by the addition of dilute sulphuric or hydrochloric acid, nickel is present. A solution containing cobalt as sesquicyanide of cobalt and potassium remains clear when mixed with an alkali and saturated with chlorine *in the cold:* if a trace of nickel be present an inky-black solution is produced. *Ferrocyanide of potassium* gives with cobalt-salts a green, *ferricyanide,* a red-brown precipitate, both insoluble in hydrochloric acid. *Alkaline phosphates* and *arsenates* give a peach-red precipitate, readily soluble in acids. *Oxalic acid* gives a pale-rose precipitate of oxalate of cobalt, which forms slowly: it is soluble in ammonia, and the oxalate separates out again on exposure to the air, but much more slowly than the oxalate of nickel. *Alkaline carbonates* precipitate a peach-red basic carbonate, readily soluble to a red solution in carbonate of ammonium, very slightly soluble in carbonate of potassium or sodium. *Potash* precipitates all the cobalt as a blue basic salt, which, if the air be excluded, is gradually converted into rose-red hydrate, CoHO; this change is facilitated by heat. In contact with the air it becomes olive-green, owing to the formation of an intermediate oxide. *Ammonia* precipitates a blue basic salt, soluble in excess to a red-brown solution. If this solution mixed with chloride of ammonium be allowed to absorb oxygen, it becomes brown; and on boiling it in strong hydrochloric acid the whole of the cobalt is precipitated as a peculiar compound, having the formula $N^5H^{16}Cl^3Co^2$. (Claudet. Chem. Soc. Qu. J. iv. 355.) If the cobalt solution contains free acid or an ammoniacal salt, ammonia produces only a red-brown solution, in which potash gives no precipitate. All soluble cobalt-salts are decomposed by heat, and after ignition are not completely soluble in water.

b. *Sesquioxide of Cobalt*, Co^4O^3 — A black powder, obtained by gently igniting the nitrate of cobalt. When heated it loses oxygen, and forms an intermediate oxide. The sesquihydrate is a black mass, obtained by passing chlorine through water in which the hydrate is suspended. Sesquichloride of cobalt is formed when a *very dilute* solution of cobalt containing no acid but hydrochloric is completely saturated with chlorine *in the cold:* from this solution carbonate of barium precipitates sesquihydrate. It is decomposed by most acids, with formation of a protosalt, and evolution of oxygen or chlorine. Acetic acid dissolves it without decomposition, forming a dark-brown solution, whence potash precipitates the sesquihydrate.

Blowpipe reactions. — Cobalt-salts are reduced when heated on charcoal with carbonate of sodium in the inner flame, cobalt being separated as a grey magnetic powder. (c) With *borax* or *microcosmic salt* they give in both flames a dark-blue bead, the colour of which is scarcely affected by the presence of any other metal.

Separation and estimation of Cobalt. — The best reactions for the qualitative detection of cobalt are the blowpipe reaction, and the difficult solubility of its sulphide in dilute hydrochloric acid, in which it is less soluble than the sulphide of nickel. The least trace of cobalt and nickel may be detected in iron-ores or other minerals by dissolving the substance in hydrochloric acid, saturating the acid solution with hydrosulphuric acid (to remove the metals of Group I.), adding sulphide of potassium to the filtrate, and washing the precipitated sulphides with cold dilute hydrochloric acid. The black residue (sulphides of nickel and cobalt) is tested for cobalt by the blowpipe, and for nickel by cyanide of potassium in its acid solution. If a large quantity of iron be present, it is best to remove it first by nearly saturating the acid solution with carbonate of sodium, and boiling with acetate of sodium. The general method for analysing cobalt-ores is the same as that described in the case of nickel (p. 143).

The separation of cobalt from *nickel* is very difficult. The best method is that given by H. Rose. The metals, or their oxides, are dissolved in hydrochloric acid, the solution very largely diluted with water, and chlorine passed through it in the cold for several hours till it is thoroughly saturated. The chloride of cobalt is thus converted into sesquichloride, the chloride of nickel remaining unchanged. Carbonate of barium is then added, and the whole allowed to stand for twelve or eighteen hours, being shaken up from time to time: and then filtered. The precipitate is washed with cold water, dissolved in boiling hydrochloric acid, freed from barium by sulphuric acid, and the cobalt precipitated by potash. The green filtrate is also treated with sulphuric acid to remove any barium it may contain, and the nickel then precipitated by potash.

Liebig's method is based on the reaction with cyanide of potassium above described. The solution of the two metals is treated with excess of potash and hydrocyanic acid (or cyanide of potassium perfectly free from cyanate) till the precipitate first formed is redissolved. The solution is boiled to expel free hydrocyanic acid, and mixed while warm with finely divided oxide of mercury, which precipitates all the nickel as hydrate and cyanide: the precipitate, when washed and ignited, yields pure oxide of nickel. The filtrate, which contains all the cobalt as sesquicyanide of cobalt and potassium, is neutralised by nitric acid, and precipitated by a neutral solution of subnitrate of mercury: the precipitate is washed, ignited, and heated in a stream of hydrogen, when pure metallic cobalt is left. Or the solution of the cyanides in cyanide of potassium may be saturated with chlorine *in the cold*, with occasional addition of caustic potash or soda: the whole of the nickel is thus precipitated as sesquihydrate, while the cobalt remains in solution.

Cobalt is best estimated in the metallic state. It is precipitated by potash as a basic salt, which is converted into the hydrate by heat: the hydrate is washed with hot water, dried, and ignited in a stream of hydrogen, and the reduced metal weighed.

3. **Manganese.** Mn. Atomic weight, 26.

Found as sesquioxide (braunite); binoxide (pyrolusite); and an intermediate oxide (Hausmannite): as sulphide, carbonate, silicate, &c.: and in most iron-ores. It is a greyish-white, brittle, difficultly fusible metal. It is readily oxidised by exposure to moist air at the ordinary temperature, forming a black powder.

OXIDES OF MANGANESE. *Protoxide*, Mn^2O. *Sesquioxide*, Mn^4O^3. *Binoxide*, Mn^2O^2. *Manganic Anhydride*, Mn^2O^3. *Permanganic Anhydride*, Mn^4O^7.—There are also two intermediate oxides, *Manganoso-manganic Oxide*, Mn^6O^4 ($Mn^2O+Mn^4O^3$), found native as *Hausmannite;* and Mn^8O^7 ($Mn^4O^3+2Mn^2O^2$), found native as *Varvicite.*

a. *Protoxide of Manganese. Manganous Oxide.* Mn^2O.—A green powder, obtained by igniting any of the higher oxides in a stream of hydrogen. It readily absorbs oxygen from the air, turning brown. It is not reduced by ignition in a stream of hydrogen. It is readily soluble in acids, forming *protosalts of manganese*, or *manganous salts,* which are either colourless or of a pale rose-colour: they are mostly soluble in water, all in hydrochloric acid, forming colourless solutions, which are not converted into manganic salts by exposure to the air or boiling with nitric acid. All the higher oxides of manganese, when heated with hydrochloric acid, evolve chlorine, and are converted into the chloride, MnCl: hence any manganese compound, after treatment with hydrochloric acid, exhibits the reactions of a manganous salt. Manganous salts are isomorphous with magnesium-salts. *Hydrosulphuric acid* does not precipitate a neutral solution of a manganous salt containing a mineral acid: even acetate of manganese is precipitated very slowly and imperfectly, and not at all if free acetic acid be present. (c) *Sulphide of ammonium* precipitates flesh-coloured sulphide, Mn^2S, readily soluble in acetic acid, absorbing oxygen and turning brown on exposure to the air. Yellow sulphide of ammonium gives a yellowish-white precipitate, which gradually becomes flesh-coloured by exposure to the air, or more rapidly on heating. *Cyanide of potassium* gives a whitish precipitate, soluble in a large excess to a brown solution, which is not precipitated by sulphide of ammonium. *Ferrocyanide of potassium* gives a reddish-white precipitate, soluble in acids: *ferricyanide of potassium*, a brown-yellow precipitate, insoluble in acids. *Alkaline phosphates*, *arsenates*, *oxalates*, and *carbonates*, give white precipitates. *Potash* precipitates white hydrate, $MnHO$, insoluble in excess: it absorbs oxygen from the air and turns brown, and is then not completely soluble in chloride of ammonium. *Ammonia* precipitates white hydrate from neutral solutions: in solutions containing free acid or ammoniacal salts, it gives no precipitate: but, if sufficient ammonia be added, the solution, on exposure to the air, gradually deposits all the manganese as brown sesquihydrate. (c) The least trace of a manganous salt is detected by heating the solution with a little *binoxide of lead* (or minium) and *nitric acid* (which must be free from hydrochloric acid), when an intense purple-red colour is produced, owing to the formation of permanganic acid: the colour is readily perceptible when the excess of lead-oxide has subsided. This is the most delicate test for manganese in the wet way.

b. *Sesquioxide of Manganese. Manganic Oxide.* Mn^4O^3.—A black powder, soluble in some acids without decomposition, forming *manganic salts*, which are isomorphous with sesquisalts of iron and aluminium. Their solution is red: *potash* precipitates from it black sesquihydrate, unless chloride of ammonium be present. They are very unstable, being reduced to manganous salts merely by heating: the same reduction is effected, and the solution decolorised, by hydrochloric, sulphurous, or nitrous acid, by any organic compound, &c. When any oxide of manganese, or a decomposable manganese-salt is heated in the air, manganoso-manganic oxide, Mn^6O^4, is formed.

c. *Binoxide of manganese*, Mn^2O^2.—This is the most important native ore of manganese. It is a black earthy powder: the hydrate is brown, and is obtained when a manganous salt is precipitated by a hypochlorite. When heated alone, or with sulphuric acid, it evolves oxygen, ($3Mn^2O^2 = Mn^6O^4 + O^2$; $Mn^2O^2 + SO^4H^2 = SO^4Mn^2 + OH^2 + O$): when heated with hydrochloric acid, it evolves chlorine ($Mn^2O^2 + 4ClH = 2MnCl + 2OH^2 + Cl^2$): with oxalic acid it evolves carbonic anhydride ($Mn^2O^2 + 2C^2O^4H^2 = C^2O^4Mn^2 + 2CO^2 + 2OH^2$). In all these reactions, a manganous salt remains in solution.

d. *Manganic Anhydride*, Mn^2O^3. *Manganic Acid*, $Mn^2O^4H^2$.—This compound has never been isolated. It is only known in a few metallic salts (*manganates*). Only the alkaline manganates are soluble in water. Manganate of potassium, $Mn^2O^4K^2$ is formed when a manganese compound is fused with excess of caustic potash or carbonate of potassium, with addition of a little nitre: it forms a green mass which dissolves in water to a green solution. On this reaction depends one of the most delicate tests for manganese (*see* Blowpipe reactions). This green solution is very unstable, rapidly becoming red on exposure to the air, owing to the formation of permanganic acid and depositing brown bihydrate: this change is retarded by the presence of excess of alkali. *Nitric*, *sulphuric*, or *hydrochloric acid* effects the change at once: with hydrochloric acid the red solution gradually becomes brown, and, when heated, colourless, manganous chloride being formed. *Sulphurous* and *hydrosulphuric acids*, and other reducing agents, decolorise the solution.

e. *Permanganic Anhydride*, Mn^4O^7. *Permanganic Acid*, $Mn^4O^8H^2$. Only known in a few metallic salts (*permanganates*), which are soluble in water, forming intense purple-red solutions. Permanganates are very readily reduced by organic compounds, and by all reducing agents (*e.g. hydrochloric*, *sulphurous*, *arsenious*, *nitrous*, *hydrosulphuric acids*, *protosalts of iron*, &c.), the solution being first turned green and finally decolorised. On its reduction by protosalts of iron, is founded a method for the volumetric estimation of iron (p. 257).

Blowpipe reactions.—(c) All manganese compounds, when finely powdered and heated on platinum-foil in the outer flame, with 2 or 3 times their weight of carbonate of sodium and a little nitre, are converted into manganate of sodium, which has a green colour when cold. If the fused mass is brown, too little nitre or too much of the manganese compound has been taken. The best way of applying the heat is to direct the hottest portion of the flame on the under-side of the platinum-foil, immediately beneath the mixture. In testing for traces of manganese in ores which are rich in iron, it is best to treat them with nitric acid, which dissolves the iron as sesquisalt, to nearly saturate the solution with carbonate of sodium, and precipitate the iron by acetate of sodium: then saturate the filtrate with ammonia, add one drop of sulphide of ammonium, and test the precipitated sulphide by fusion with nitre and carbonate of sodium. With *borax* and *microcosmic salt* all manganese compounds give in the outer flame a clear amethyst bead, which is rendered colourless in the inner flame. The amethyst colour is most distinct in the borax bead: and the decolorisation in the inner flame is most easily effected in the microcosmic bead. If so little manganese be present that the amethyst colour cannot be perceived, the microcosmic bead should be heated in the outer flame, and brought into contact while still hot with a crystal of nitre, when it swells up to a spongy mass of a violet colour.

Separation and estimation of Manganese.—Manganese is separated from the metals of Group I. by the non-precipitation of its sulphide from an acid solution. Its separation from *cobalt* and *nickel* is not easy. The best method is to convert the mixed oxides into chlorides by ignition in a stream of chlorine, and to ignite the mixed chlorides in a stream of hydrogen, when the cobalt and nickel are reduced to the metallic state, while the chloride of manganese remains unaltered, and may be dissolved out by water. An easier and tolerably accurate method is to separate them by hydrosulphuric acid. The solution, which must not contain much free acid, is mixed with acetate of sodium and saturated with hydrosulphuric acid, when the sulphides of cobalt and nickel are precipitated, while the sulphide of manganese remains dissolved. Or the mixed oxides are converted into sulphides by ignition in a stream of hydrosulphuric acid, and the mixed sulphides treated with very dilute cold hydrochloric acid, which dissolves the sulphide of manganese only. The separation by either of these methods may be rendered almost absolute by repeating the process two or three times.

Manganese is estimated as manganoso-manganic oxide, Mn^6O^4. It is precipitated by carbonate of sodium, the precipitate washed with hot water, dried and ignited, by which means it is converted into pure Mn^6O^4, and so weighed.

4. **Iron.** Fe. Atomic weight, 28.

One of the most abundant of the metals. It is found combined with oxygen, as ferroso-ferric oxide (magnetic iron-ore), and as sesquihydrate or sesquioxide (red and brown hæmatite, specular iron-ore, &c.): as bisulphide (iron-pyrites): as carbonate (spathic iron-ore): and in many other combinations. It is a greyish-white metal, highly magnetic. It is not oxidised by dry air at the ordinary temperature: but in moist air it is gradually converted into sesquihydrate. Heated in the air, it becomes covered with a film of black oxide. It is readily soluble in dilute acids; but nitric acid of a certain strength does not dissolve it under certain circumstances.

OXIDES OF IRON. *Protoxide*, Fe^2O. *Sesquioxide*, Fe^4O^3. *Ferric Anhydride*, Fe^2O^3. — There is also an intermediate oxide between the protoxide and the sesquioxide, which is in fact a compound of these two oxides: its formula is Fe^6O^4: it is generally called *Ferroso-ferric Oxide* or *Magnetic Oxide.*

a. *Protoxide of Iron. Ferrous Oxide.* Fe^2O.—Not known in the separate state. The hydrate, FeHO, is precipitated white by alkalis from a protosalt of iron: it is very difficult to obtain it pure, as it oxidises rapidly by exposure to the air: when dried it has a green colour, probably owing to partial oxidation. *Protosalts of iron*, or *ferrous salts*, are formed by dissolving iron in acids. They are white when anhydrous; but bluish-green when in solution, or when they contain water of crystallisation. They are decomposed by heat, losing their acid, and being converted into red-brown sesquioxide. Even in the solid state they absorb oxygen from the air: in solution the oxidation is much more rapid, a yellow basic sesquisalt separating out, while the solution contains both proto- and sesquisalt. This solution is readily and completely converted into a sesquisalt by boiling with nitric acid; or, in the cold, by chlorine, hypochlorous acid, or hydrochloric acid and chlorate of potassium. The first action of nitric acid is to produce a dark-brown solution, owing to nitric oxide being dissolved in the unoxidised portion of the ferrous salt: on adding more nitric acid, or on heating, so as to oxidise the whole of the ferrous salt, the dark-brown colour disappears, nitric oxide being evolved. In order to avoid the separation of a basic sesquisalt in this reaction, half as much free acid as is already contained in the ferrous salt must be added to the solution.

Hydrosulphuric acid does not precipitate neutral or acid solutions of ferrous salts: even acetate of iron is only partially precipitated. *Sulphide of ammonium* precipitates all the iron as black sulphide, Fe^2S, insoluble in excess unless a large quantity of carbonate of sodium be present, in which case it is slightly soluble. It is readily soluble in dilute hydrochloric acid, hydrosulphuric acid being evolved, and protochloride, FeCl, formed. It readily absorbs oxygen from the air and turns brown: hence it must be washed with water from which the air has been expelled by boiling, and to which a few drops of sulphide of ammonium have been added. (c) *Ferrocyanide of potassium* gives a white precipitate, Cy^6Fe^5K, insoluble in hydrochloric acid: by the action of the air or of any oxidising agent, it is rapidly converted into prussian blue, Cy^9Fe^7. Potash decomposes both these compounds, separating ferrous hydrate in the first case, and ferric hydrate in the second. (c) *Ferricyanide of potassium* gives a dark-blue precipitate of Cy^6Fe^5, insoluble in hydrochloric acid, decomposed by alkalis. These precipitates do not form in an alkaline solution. *Gallic acid* gives no precipitate with pure ferrous salts. *Terchloride of gold* and *nitrate of silver* are reduced by ferrous salts, with separation of metallic gold and silver. *Oxalic acid* precipitates yellow ferrous oxalate, insoluble in excess, soluble in hydrochloric acid. *Alkaline phosphates* and *carbonates* give white precipitates, which become dirty-green by exposure to the air. *Caustic alkalis* precipitate white hydrate, which becomes green and finally red-brown by exposure to the air. It is soluble in chloride of ammonium: hence ammonia gives no precipitate in a ferrous solution containing sufficient chloride of ammonium; but when the solution is exposed to the air, red-brown flakes of ferric hydrate gradually separate out.

b. *Sesquioxide of Iron. Ferric Oxide.* Fe^4O^3.—A brown powder, obtained by igniting, at a moderate red heat, the sesquihydrate obtained by precipitating a ferric salt by ammonia. At a white heat it loses oxygen, and is converted into ferroso-ferric oxide, Fe^6O^4. It is soluble in acids (more slowly after ignition), forming *sesquisalts of iron*, or *ferric salts.* Their aqueous solution is orange-red, and reddens litmus: if it contains free acid, it is yellow, but becomes red on boiling. On boiling a very dilute aqueous solution, almost all the iron separates as an insoluble basic salt. *Hydrosulphuric acid* reduces ferric salts to ferrous salts, with separation of sulphur, which renders the solution milky ($2Fe^2Cl^3 + SH^2 = 4FeCl + 2ClH + S$). The same reduction is effected by heating a ferric salt with metallic *iron* or *zinc* ($Fe^2Cl^3 + Fe = 3FeCl$) or with *sulphurous acid* ($2Fe^2Cl^3 + SO^3H^2 + OH^2 = 4FeCl + 2ClH + SO^4H^2$). *Sulphide of ammonium* also reduces ferric salts, and precipitates protosulphide, Fe^2S, mixed with sulphur, which is left undissolved on addition of hydrochloric acid. (C) *Ferrocyanide of potassium* precipitates prussian blue, Cy^9Fe^7 ($3Cy^3FeK^2 + 2Fe^2Cl^3 = Cy^9Fe^7 + 6ClK$), insoluble in hydrochloric acid, decomposed by potash into ferrocyanide of potassium and ferric hydrate. *Ferricyanide of potassium* gives no precipitate or change of colour, unless a trace of protosalt be present, in which case a dark-coloured solution is produced. (C) *Sulphocyanate of potassium* gives a dark-red colour even in very dilute ferric solutions, which is not destroyed by hydrochloric acid, but disappears on the addition of chloride of mercury, or of tartaric or phosphoric acid, and is partially reproduced on addition of hydrochloric acid. *Gallic acid* gives a bluish-black precipitate, soluble in free acids. *Oxalate of potassium* precipitates yellow ferric oxalate, soluble in free oxalic acid. *Phosphate* or *arsenate of sodium* gives a white precipitate of ferric phosphate or arsenate, insoluble in acetic acid, soluble in ferric acetate or chloride, or in ammonia in presence of excess of phosphate of sodium. *Carbonate of barium* precipitates ferric salts completely in the cold: *benzoate* or *succinate of ammonium* also precipitates all the iron from a neutral ferric solution. These reagents do not precipitate ferrous salts at all in the cold. *Caustic alkalis* and *alkaline carbonates* precipitate red-brown ferric hydrate, insoluble in excess, (except in excess of carbonate of ammonium,) even in presence of ammoniacal salts. The precipitate always contains some alkali, which cannot be entirely removed by washing. Non-volatile organic bodies (*e.g.* tartaric acid, sugar, &c.) hinder this precipitation, but not that by sulphide of ammonium. Soluble ferric salts are decomposed by ignition in the air.

The reactions with ferro- and ferricyanide of potassium, and with sulphocyanate of potassium, enable us to detect ferrous and ferric salts in presence of each other. Their separation is effected by carbonate of barium in the cold, or by benzoate or succinate of ammonium in a perfectly neutral solution (the air being excluded as far as possible) which precipitates ferric salts completely, while ferrous salts remain in solution. The best way to obtain a perfectly neutral solution is to add ammonia drop by drop, continually stirring the solution, until the slightest possible permanent precipitate is formed.

Ferroso-ferric Oxide, or *Magnetic Oxide*, Fe^6O^4 (as well as another intermediate oxide, known as *Scale-oxide*, $Fe^{16}O^9$, obtained by heating iron to redness, in contact with the air) is soluble in hydrochloric acid: caustic alkalis precipitate black ferroso-ferric hydrate from this solution. In other respects the solution behaves like a mixture of ferrous and ferric chloride.

c. *Ferric Anhydride*, Fe^2O^3. *Ferric acid*, $Fe^2O^4H^2$ —This compound has never been obtained in the separate state. It is only known in its alkaline salts, which are obtained in the same way as the manganates. Their solution is of a fine red colour: they are reduced even more readily than the manganates, with separation of ferric hydrate.

Blowpipe reactions.—All iron-salts are reduced when heated on charcoal with carbonate of sodium in the inner flame, metallic iron being obtained as a magnetic powder. With *borax* they give in the outer flame a bead which, according to the quantity of iron-salt present, is red or yellow when hot, yellow or colourless when cool: in the inner flame they give a bottle-green bead.

With *microcosmic salt* they give in the outer flame a bead which is yellowish-red when hot, colourless when cool: in the inner flame no coloration is produced unless a considerable quantity of iron-salt be employed, when the bead is red while hot, and reddish when cool.

Separation and estimation of Iron.—Most native compounds of iron are dissolved by concentrated hydrochloric acid; some require the addition of nitric acid. Iron-scoriæ, which consist of ferrous silicates, are decomposed by hydrochloric acid: ferric silicates, which are not attacked by acids, are fused with carbonate of potassium and sodium. For the detection of the foreign elements contained in cast-iron (which seldom amount to more than 5 p. c.) the residue left after dissolving the iron in dilute sulphuric acid is usually employed: it contains generally silicon, carbon, carbide, phosphide, and arsenide of iron, chromium, vanadium, molybdenum, and sometimes cobalt.

Iron is separated from the metals of Group I. by the non-precipitation of its sulphide from an acid solution. For its separation from *nickel*, *cobalt*, and *manganese*, the following is the best process. The solution of the metals in hydrochloric acid is thoroughly saturated with chlorine, in order to convert the whole of the iron into sesquisalt, and then boiled, in order to reduce to protosalts any sesquisalts of the other metals which may have been formed. The solution is then carefully neutralised with ammonia, chloride of ammonium having been added in order to prevent the precipitation of any of the protoxides. (If the solution be very acid, sufficient ammoniacal salt will be formed in the process of neutralisation.) Succinate of ammonium is then added, which precipitates the iron alone as ferric succinate: the precipitate is washed, dried, and ignited in an open platinum crucible, with full access of air, in order to prevent any reduction of iron by the carbon of the organic acid. Should any iron be so reduced, it must be reoxidised by nitric acid. The sesquioxide of iron is then weighed. The success of this method depends on the exact neutralisation of the solution: this is ensured by adding ammonia drop by drop to the point when a permanent precipitate is first formed. The iron may be precipitated by carbonate of barium in the cold, instead of by succinate of ammonium: the precipitate is dissolved in hydrochloric acid, the barium removed by sulphuric acid, and the iron thrown down by ammonia. In the case of *cobalt*, however, carbonate of barium does not answer so well as succinate of ammonium.

Iron is always estimated as sesquioxide. It is precipitated by ammonia as sesquihydrate, which, when dried and ignited, leaves pure sesquioxide. If potash be employed as the precipitant, the precipitate always contains some alkali, which cannot be removed by washing, but only by dissolving the sesquioxide in hydrochloric acid, and reprecipitating by ammonia. If any organic matter be present, which would prevent the precipitation of ferric oxide by ammonia, the iron must be precipitated as sulphide, the sulphide dissolved in nitric acid, and the solution precipitated by ammonia.

5. **Zinc.** Zn. Atomic weight, 32·5.

Found chiefly as sulphide (zinc-blende): as carbonate (calamine): as silicate (zinc-glance). It is a bluish-white metal, malleable when pure, easily fusible. It is not oxidised by dry air at the ordinary temperature: in contact with water and air containing carbonic acid it is gradually converted into a mixture of hydrate and carbonate of zinc. Heated in the air it burns with a bright bluish flame, forming oxide of zinc. It is volatile, and may be distilled. It is soluble not only in mineral acids, but even in many organic acids: also, to a certain extent, in caustic alkalis.

Oxide of Zinc. *Zinc-oxide*, Zn^2O.—A white powder, obtained by the combustion of the metal in the air. When heated, it assumes a yellow tinge, but becomes white again on cooling. It is not volatile. It is readily soluble in acids, forming *zinc-salts:* soluble also in alkalis. Zinc-salts are colourless, and give colourless solutions. *Hydrosulphuric acid* gives with neutral solutions of zinc-salts a white precipitate of sulphide, which does not contain all the zinc: in solutions containing sufficient free hydrochloric acid there is no precipitate. Acetate of zinc, or any zinc solution mixed with acetate of sodium, is completely precipitated by hydrosulphuric acid, even if a large quantity of free acetic acid is present. Sulphide of zinc is insoluble in caustic alkalis. *Sulphide of ammonium* precipitates zinc solutions completely. *Cyanide of potassium* precipitates white cyanide, soluble in excess, not reprecipitated by sulphide of ammonium. *Ferrocyanide of potassium* gives a white precipitate, insoluble in hydrochloric acid. *Oxalic acid* and *phosphate of sodium* precipitate white oxalate and phosphate, soluble in acids and alkalis: the phosphate is not precipitated in presence of chloride of ammonium and ammonia. *Fixed alkaline carbonates* precipitate a white basic carbonate, insoluble in excess, soluble in alkalis: chloride of ammonium hinders this precipitation in the cold. *Potash*, *ammonia*, and *carbonate of ammonium* give white precipitates, soluble in excess, reprecipitated on diluting with water and boiling: soluble also in chloride of ammonium. (c) Hydrosulphuric acid precipitates the sulphide from these solutions. Most zinc-salts are decomposed by heat, zinc-oxide being left.

Blowpipe reactions.—All zinc compounds, when heated on charcoal with carbonate of sodium in the inner flame, give an incrustation of zinc-oxide, which is yellow while hot, but white on cooling: it is not volatile in the outer flame. With *borax* or *microcosmic salt* they give in both flames a bead which is yellowish while hot, white on cooling, and opaque if much zinc-salt be present. If the colourless bead, or the white incrustation, be moistened with a dilute solution of nitrate of cobalt, and strongly heated in the outer flame, a fine green colour is produced.

Separation and estimation of Zinc.—All zinc-ores are decomposed by digestion in hydrochloric acid, except the sulphide, which requires aqua-regia. The qualitative detection of zinc is very easy: the precipitation of the solution of its hydrate in an alkali by sulphide of ammonium is quite characteristic of zinc.

From the metals of Group I. zinc is separated by the non-precipitation of its sulphide from an acid solution. From *iron*, by succinate of ammonium, or carbonate of barium, as described in the case of manganese (p. 157). From *manganese* by converting the metals into acetates, adding free acetic acid, and saturating with hydrosulphuric acid, which precipitates the sulphide of zinc only. If any mineral acids be present in the solution, they must be removed by precipitating the metals by carbonate of sodium, and dissolving the washed precipitate in acetic acid; or, if the acids are volatile, by boiling the solution with sulphuric acid, and decomposing the sulphates thus formed by acetate of barium. From *cobalt* and *nickel*, zinc may be separated in the same manner as from manganese, but the quantity of free acetic acid must be very large: or the mixture of the three oxides (obtained by adding carbonate of sodium to their solution, evaporating to dryness, extracting with water, and washing and igniting the residue) may be heated in a stream of dry hydrogen as long as any water is formed, when the cobalt and nickel are reduced to the metallic state, while the oxide of zinc remains undecomposed and may be dissolved out by digestion in a concentrated solution of carbonate of ammonium. Zinc may also be separated from *cobalt* and *manganese* by the conversion of the latter metals into sesquisalts by saturating their solution with chlorine, and then precipitating them by carbonate of barium in the cold. Zinc may be separated from *nickel* by mixing the concentrated solution with excess of potash and then with hydrocyanic acid, so that the two metals are dissolved as double cyanides. From this solution sulphide of potassium (not sulphide of ammonium) completely precipitates the zinc as sulphide: the filtrate is boiled with aqua-regia, and the nickel precipitated by ammonia as hydrate.

Zinc is estimated as oxide. It is precipitated by boiling with excess of carbonate of sodium: or, as a basic salt may be formed in this way, it is better to pour the zinc solution into the boiling alkaline carbonate. The precipitate, when washed, dried, and ignited, yields zinc-oxide. If the zinc solution contains ammoniacal salts, they must be removed by boiling with enough alkaline carbonate to decompose them, evaporating to dryness as quickly as possible, dissolving out the soluble salts in a large quantity of water, and collecting the residual carbonate of zinc on a filter. When zinc is precipitated by sulphide of ammonium, the solution, if acid, must first be neutralised by ammonia: the sulphide must be allowed to subside before filtration, as otherwise it would stop up the filter: it is then washed with water containing a little sulphide of ammonium, dissolved in hydrochloric acid, and the

6. **Uranium.** U. Atomic weight, 60.

Occurs, not abundantly, as impure uranoso-uranic oxide (pitch-blende): as uranic hydrate (uran-ochre): as phosphate of uranium and copper (uranite), &c. It is generally obtained as a black powder, occasionally in small compact plates, of a silvery lustre and slightly malleable. It is not oxidised by the air at the ordinary temperature. Heated in the air it burns vividly, forming green uranoso-uranic oxide.

OXIDES OF URANIUM. *Protoxide*, U^2O. *Sesquioxide*, U^4O^3.—There is also an intermediate oxide, uranoso-uranic oxide, U^6O^4, which is a compound of protoxide and sesquioxide.

a. *Protoxide of Uranium. Uranous Oxide.* U^2O.—A grey powder, obtained from uranoso-uranic oxide by igniting it in a stream of hydrogen, or by heating it strongly in a blast-furnace in contact with charcoal: also by reducing uranic oxalate by hydrogen. The oxide is soluble only in strong sulphuric or nitric acid. The hydrate, UHO, is soluble in acids, forming *uranous salts*. These are green: in solution they are readily converted into uranic salts by exposure to the air or by treatment with nitric acid. *Sulphide of ammonium* precipitates from them black uranous sulphide: *caustic alkalis* precipitate red-brown uranous hydrate.

b. *Sesquioxide of Uranium. Uranic Oxide.* U^4O^3.—A brick-red powder, obtained by heating yellow uranic hydrate to about 300°. When ignited it loses oxygen and is converted into uranoso-uranic oxide. The hydrate is soluble in acids, forming *uranic salts*, which are yellow and mostly soluble in water to yellow solutions. Uranic oxide also forms compounds with alkalis. *Hydrosulphuric acid* gives no precipitate with uranic salts, but reduces them to uranous salts; the same reduction is effected by *alcohol* or *ether* in the sunshine. *Sulphide of ammonium* precipitates brown uranic sulphide, insoluble in excess, which deposits very slowly. *Ferrocyanide of potassium* gives a red-brown precipitate, which is decomposed by caustic potash into ferrocyanide of potassium and a yellow compound of uranic oxide with potash. *Phosphate* and *arsenate of sodium* and *oxalic acid* give yellowish-white precipitates, unless much free acid is present. *Succinate of ammonium* or *carbonate of barium* precipitates uranic salts completely in the cold. *Alkaline carbonates* give pale yellow precipitates, soluble in excess, especially of carbonate of ammonium, reprecipitated by potash, or by boiling the solution. *Caustic alkalis* precipitate yellow compounds of uranic oxide with the alkali, insoluble in excess. Metallic *zinc* does not reduce metallic uranium from uranic salts, but after a long time produces a yellow precipitate of uranic oxide. Soluble uranic salts are decomposed by ignition in the air.

Uranoso-uranic Oxide, U^6O^4, is a green powder, obtained by igniting uranic oxide, or burning the metal in the air. It is soluble in acids, forming green solutions, whose reactions are intermediate between those of uranous and uranic salts.

Blowpipe reactions.—Uranic oxide is not dissolved or reduced when heated on charcoal with carbonate of sodium in the inner flame. With *borax* and *microcosmic salt* it gives in the outer flame a clear bead, which is yellow while hot, yellowish-green on cooling: in the inner flame the bead is green when hot, and a still purer green when cool.

Separation and estimation of Uranium.—Uranium is detected qualitatively by its precipitation by sulphide of ammonium and by alkalis, even in presence of chloride of ammonium: and by the solubility of uranic hydrate in carbonate of ammonium, by which it is distinguished from iron.

For the extraction of uranium from pitchblende (which generally contains also silica, iron, nickel, cobalt, zinc, copper, bismuth, lead, manganese, arsenic, antimony, calcium, magnesium, sulphur, and sometimes selenium and vanadium), the finely-powdered mineral is digested with moderately dilute sulphuric acid with gradual addition of nitric acid, till it is converted into a white powder: the excess of acid is then driven off, the residue digested in cold water, and the solution filtered. The residue contains silica, sulphate of lead, and basic sulphate and arsenate of bismuth. The solution, heated to about 60°, is saturated with hydrosulphuric acid, and allowed to stand for twenty-four hours: it is then heated to expel the excess of the gas, and the sulphides of arsenic, antimony, copper, lead, and bismuth, filtered off. The filtrate is heated to boiling, and nitric acid gradually added till all the iron is converted into sesquisalt, and the solution is yellow, when it is precipitated by excess of ammonia and filtered. The precipitate, besides ferric and uranic oxides, contains traces of nickel, cobalt, zinc, magnesium, and calcium: the rest of these metals is in the filtrate. The precipitate is washed, and digested with a concentrated solution of carbonate of ammonium, until it has the pure red-brown colour of ferric hydrate: it is then filtered while warm, and the filtrate on cooling deposits crystals of carbonate of uranium and ammonium, which on ignition yield uranoso-uranic oxide. The mother-liquor from these crystals is then treated by sulphide of ammonium, drop by drop, as long as a dark-brown precipitate (sulphides of cobalt, nickel, and zinc) is produced; it is then filtered, and the filtrate boiled for a long time, when all the uranium is precipitated as uranate of ammonium, which on ignition yields uranoso-uranic oxide. The ferric hydrate still retains traces of uranium, which may be separated by dissolving the whole in as little hydrochloric acid as possible, neutralising with carbonate of ammonium, and pouring the solution into a mixture of carbonate and sulphide of ammonium, when the iron is precipitated as sulphide, while the uranium remains in solution. For the detection of selenium and vanadium the powdered ore is fused with a quarter of its weight of nitre and carbonate of sodium, and the fused mass treated with water, which dissolves out the alkaline selenates, vanadates, and arsenates.

Uranium is separated from the metals of Group I. by the non-precipitation of its sulphide from acid solutions. From *nickel*, *cobalt*, *manganese*, and *zinc*, it is separated by saturating the solution with chlorine, boiling, and precipitating by carbonate of barium in the cold, which carries down the uranium only. From *iron* by neutralising the solution with ammonia, diluting with water, and adding normal carbonate of ammonium (freed from excess of carbonic acid by boiling), which precipitates only the iron, the uranium remaining in solution.

Uranium is estimated as uranoso-uranic oxide, or as protoxide. It is precipitated by ammonia, washed with water containing chloride of ammonium, dried, and converted by ignition into uranoso-uranic oxide, which is allowed to cool in a covered crucible and weighed. Or the precipitate is reduced by ignition in a stream of hydrogen, and weighed as uranous oxide. If the uranium solution contain much of a fixed alkali or alkaline earth, the precipitate by ammonia will carry down with it some of the alkali or earth, which cannot be removed by ignition: in this case it must be dissolved in hydrochloric acid, and reprecipitated by ammonia.

Group II.—Subdivision B.

The metals of this group do not combine with sulphur in the wet way, and consequently are not precipitated by hydrosulphuric acid under any circumstances. Their oxides, however, being insoluble in water or ammoniacal salts, are precipitated from their neutral or acid solutions by sulphide of ammonium, the acid by which they were held in solution being neutralised by the ammonia of the reagent, while the hydrosulphuric acid escapes.*

The oxides of some of the metals in this group are known as *earths:* hence these metals are called *earthy-metals.* The earths are white, yellowish, or brownish powders, infusible, generally exhibiting a vivid incandescence on ignition: they have no alkaline reaction, are insoluble in water, and after ignition are difficultly soluble in acids. They cannot be reduced to the metallic state by heating in contact with hydrogen or charcoal. Sulphide of ammonium, ammonia, and fixed alkalis throw them down from their salts as gelatinous precipitates.

1. **Aluminium.** Al. Atomic weight, 13·6.

One of the most abundant of the metals. It occurs chiefly in combination with silica, in clays, and several minerals: also with sulphuric, phosphoric, and other acids. It is a white, very light

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* Or we may suppose a sulphide to be first formed and then decomposed by water—

$$2Al^2Cl^3 + 3(NH^4)^2S = Al^4S^3 + 6NH^4Cl.$$
$$Al^4S^3 + 3H^2O = Al^4O^3 + 3H^2S.$$

metal, which does not oxidise in the air even at a strong red heat. It is insoluble in cold, very slowly soluble in boiling, nitric acid: insoluble in cold dilute sulphuric acid: readily soluble in hydrochloric acid.

Oxide of Aluminium. *Alumina*, Al^4O^3.—A white powder, prepared by igniting the hydrate: at a strong red heat it fuses to a solid, very hard, mass. It is soluble in acids before ignition, but not very readily; the hydrate is readily soluble in acids, forming *salts of aluminium*. These are colourless, unless their acid is coloured: those which are soluble in water give solutions which redden litmus. Those which are insoluble in water are mostly soluble in hydrochloric acid. Many native aluminium compounds, which cannot be decomposed by hydrochloric acid, are dissolved by boiling with strong sulphuric acid: all are decomposed by fusion with acid sulphate of potassium, or an alkaline carbonate. *Sulphide* and *carbonate of ammonium* give with aluminium-salts a white gelatinous precipitate of hydrate, insoluble in excess: the *fixed alkaline carbonates* and *ammonia* give the same precipitate, somewhat soluble in a large excess. *Phosphate of sodium* precipitates phosphate of aluminium, very closely resembling the hydrate in appearance, and like it soluble in potash and in acids (not in hot acetic acid). Chloride of ammonium reprecipitates the phosphate from the potash solution: alkaline silicates precipitate silicate of aluminium from the potash solution either of the phosphate or hydrate, the phosphoric acid in the former case remaining in solution. Chloride of barium or baryta-water added to the potash solution of phosphate of aluminium, precipitate all the phosphoric acid as phosphate of barium, while, if excess of potash be added and the whole heated, the alumina remains in solution. (c) When *acid sulphate of potassium* is added to a hot concentrated solution of an aluminium-salt, the solution on cooling deposits octahedral crystals of *alum* (sulphate of aluminium and potassium). *Oxalic acid* and soluble *oxalates* give no precipitate with aluminium-salts. *Carbonate of barium* in the cold precipitates all the alumina very slowly. *Potash* or *soda* precipitates the hydrate, readily soluble in excess, reprecipitated by chloride of ammonium in sufficient quantity, or by neutralisation with hydrochloric acid and saturation with ammonia. The alkaline solution is not precipitated by sulphide of ammonium. The aluminium-salts of volatile acids are decomposed by ignition, losing their acid.

Blowpipe reactions.—When an aluminium compound is heated on charcoal, moistened with nitrate of cobalt, and again heated, a fine blue colour is produced.

Separation and estimation of Aluminium.—From the metals of Group I. aluminium is separated by hydrosulphuric acid in an acid solution. It cannot be separated by potash from those metals whose hydrates are insoluble in potash, except in cases where the insoluble hydrate is present in very small proportion (not more than 1 p. c.): for in other cases the insoluble hydrate always retains some alumina. From *cobalt*, *nickel*, *manganese*, and *zinc* it is best separated by carbonate of barium in the cold, when these metals, being in the form of protosalts, are not precipitated. For its separation from *iron* and *uranium*, the metals are precipitated together by sulphide of ammonium, and the precipitate boiled in caustic potash, and filtered. The residue, which still contains alumina, is dissolved in hydrochloric acid, again super-saturated with potash, boiled, and filtered: and this process must be repeated until the alkaline filtrate gives no precipitate with sulphate of ammonium. The alkaline solution of alumina is then neutralised with hydrochloric acid and precipitated by sulphide of ammonium. A better method for the separation of aluminium from *iron* is to heat the acid solution to boiling, and add sulphite of sodium or sulphurous acid, in order to reduce the iron to protosalt, to neutralise with carbonate of sodium, and then to boil with excess of caustic soda until the white precipitate of hydrate of iron is converted into black ferroso-ferric oxide, which is filtered off and the alumina precipitated as before by sulphide of ammonium.

Chancel (Compt. rend. xlvi. 987) states that iron and aluminium may be completely separated by hyposulphite of sodium, which merely reduces ferric salts to ferrous salts; but precipitates alumina from salts of aluminium, being itself decomposed in the usual manner by the acid of the aluminium-salt ($2Al^2Cl^3 + 3S^2O^3Na^2 = Al^4O^3 + 6NaCl + 3SO^2 + S^3$). The iron and aluminium being both in the form of sesquisalt, their solution is nearly neutralised (if necessary) with sodic carbonate, and *largely diluted** with water. A slight excess of hyposulphite of sodium is added in the cold; (if it be added to a hot solution some ferric hydrate would be precipitated;) and the whole boiled as long as sulphurous anhydride is evolved. The precipitated alumina, which is pulverulent, not gelatinous, is filtered off, washed, freed from sulphur by heating moderately, ignited, and weighed. The filtrate containing all the iron is concentrated by evaporation, and boiled with hydrochloric acid and chlorate of potassium till the separated sulphur is bright yellow, and begins to agglomerate: it is then diluted, filtered from the sulphur which is thoroughly washed, and precipitated by ammonia.

Aluminium is always estimated as alumina. It is precipitated as hydrate by sulphide of ammonium (which is better than ammonia or carbonate of ammonium): if the solution contain any alkaline-earthy metals, the access of air must be prevented as far as possible, otherwise these metals may be partly precipitated as carbonates. The hydrate, when dried and ignited, yields pure alumina, Al^4O^3.

2. **Glucinum** or **Beryllium**. G. Atomic weight, 4·7.

A rare metal, found chiefly as silicate, in some minerals. It is a white very light metal, which, when heated in the air or in oxygen, becomes coated with a thin film of oxide, which protects it from further change. It is soluble in hydrochloric or sulphuric acid: insoluble in cold, slowly soluble in boiling, nitric acid: soluble in potash, but not in ammonia. (Debray. Ann. Ch. Phys. [3.] xliv. 5).

Oxide of Glucinum. *Glucina*, G^2O.—A white powder, obtained by igniting the carbonate. It is soluble in acids, forming *salts of glucinum.* These closely resemble aluminium-salts in their reactions: there are, however, the following differences between them. *Acid sulphate of potassium* forms no crystals with glucinum-salts: neither does *carbonate of barium* precipitate them in the cold. *Alkaline carbonates* precipitate carbonate of glucinum, soluble in excess (especially of carbonate of ammonium): the solution is reprecipitated on boiling. *Potash* precipitates hydrate of glucinum, soluble in excess, reprecipitated on prolonged boiling. Hydrate of glucinum is soluble in boiling chloride of ammonium, ammonia being evolved. When treated with *nitrate of cobalt* before the blowpipe, glucinum-salts give, not a blue, but a grey colour.

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* 50 cc. solution should not contain more than 0·1 grm. alumina.

Separation and estimation of Glucinum.—Native glucinum-compounds (beryl, emerald, euclase, phenacite, &c.) are completely decomposed by fusion with three or four times their weight of carbonates of potassium and sodium.

Glucinum is separated from all the preceding metals in the same manner as aluminium. From *iron* it may also be separated by carbonate of barium. From *aluminium* it is separated by carbonate of ammonium; or by boiling the potash solution of the two hydrates; or by carbonate of barium.

3. **Zirconium.** Zr. Atomic weight, 22·4.

A rare metal, found as silicate in some minerals (zircon, &c.). It is obtained as a black powder, which burns with a bright flame when heated in the air. It is scarcely soluble in any acids except hydrofluoric acid.

OXIDE OF ZIRCONIUM. *Zirconia*, Zr^2O.—A white powder, obtained by the combustion of zirconium in the air; also by igniting the hydrate. After ignition it is soluble in no acids but strong boiling sulphuric acid. The hydrate is readily soluble in acids, forming *zirconium-salts. Sulphate of potassium* precipitates a white sulphate of zirconium and potassium, insoluble in water, and, if precipitated from a hot solution, insoluble in hydrochloric acid. *Oxalic acid* precipitates white oxalate, insoluble in excess, difficultly soluble in hydrochloric acid. *Alkalis and alkaline carbonates* give white precipitates insoluble in excess, except in excess of carbonate of ammonium: the solution is reprecipitated on boiling.

Separation and estimation of Zirconium. — Native zirconium compounds are decomposed by fusion with carbonate of sodium. The fused mass is treated with water, which dissolves the alkaline silicate, leaving a crystalline residue of silicate of zirconium and sodium, from which the silica is removed by evaporation to dryness with hydrochloric acid. After filtering off the silica, the zirconium is precipitated as hydrate by ammonia.

From most of the preceding metals of this group, zirconium may be approximately separated by the solubility of its hydrate in carbonate of ammonium. From *aluminium* it may be separated by potash. From *manganese* by ammonia in presence of chloride of ammonium. From *glucinum*, according to Berthier, by suspending the hydrates in water, passing sulphurous anhydride into them till they are completely dissolved, and boiling the solution: when the zirconium is precipitated as a basic sulphite, while the glucinum remains dissolved. None of these separations are complete.

Zirconium is estimated as oxide. It is precipitated as hydrate by ammonia, and the precipitate on ignition yields pure zirconia.

4. **Thorium.** Th. Atomic weight, 59·5.

A very rare metal, only found in thorite, monacite, and pyrochlorite. It is obtained as a black powder, which burns brilliantly when heated in the air. It is most soluble in hydrochloric acid.

OXIDE OF THORIUM. *Thoria.* Th^2O.—A white powder, obtained by the combustion of the metal in the air, or by igniting the hydrate. After ignition it is soluble only in strong boiling sulphuric acid. The hydrate is readily soluble in acids, forming *thorium-salts*, which closely resemble zirconium-salts in their reactions. The double sulphate of thorium and potassium differs from the corresponding zirconium-salt by being soluble in hot water. It is insoluble in a saturated solution of sulphate of potassium.

Separation and estimation of Thorium.—Thorium may be separated from the preceding metals, except zirconium, by completely saturating their solution with sulphate of potassium. The precipitate is dissolved in hot water, and the thorium precipitated as hydrate by ammonia. From *aluminium* and *glucinum* it is also separated by potash. No method is known for separating it from zirconium.

Thorium is estimated as oxide. It is precipitated by ammonia as hydrate, which on ignition yields pure oxide.

Thorite is completely decomposed by digestion with concentrated hydrochloric acid.

5. **Yttrium.** Y. Atomic weight, 35.
Terbium. Tr. } Atomic weight not determined.
Erbium. E. }

These very rare metals exist in a few minerals (gadolinite, orthite, yttrotantalite). They are scarcely known in the metallic state. Their oxides, *yttria*, Y^2O, *terbia*, Te^2O, and *erbia*, E^2O, always occur together, and no method for their separation is known. They differ from most other earths in being readily soluble in acids after ignition. Yttria and terbia are white: erbia is dark-yellow. They are insoluble in *fixed alkalis*: soluble in *carbonate of ammonium*, but less readily than glucina. *Oxalic acid* gives a white precipitate with their salts, insoluble in water. *Acid sulphate of potassium* precipitates a double salt, slowly soluble in a large quantity of water, more soluble in a saturated solution of sulphate of potassium. *Carbonate of barium* does not precipitate them, either in the cold or on heating.

Separation and estimation of Yttrium.—Yttrium is separated from *aluminium* by carbonate of barium. From *glucinum* by oxalic acid: or better, by calcining the earths with some organic body (*e.g.* sugar) and heating the mixture in a stream of chlorine, when chloride of glucinum volatilises, while chloride of yttrium remains behind. No method is known for its separation from *zirconium* and *thorium*. Ammonia precipitates erbia before terbia, and terbia before yttria: but no complete separation can thus be effected.

Yttrium is estimated as oxide, obtained by igniting the hydrate precipitated by ammonia.

6. **Cerium.** Ce. Atomic weight, 46.
Lanthanum. La. Atomic weight, 46.
Didymium. Di. Atomic weight, 48.

These rare metals are always found together: they occur in a few metals, iron, and calcium. Little is known of them in the metallic state, except that they dissolve readily in acids.

Oxides of Cerium. *Protoxide*, CeO. *Sesquioxide*, Ce^2O^3.

a. *Protoxide of Cerium. Cerous Oxide.* Ce^2O.—It is doubtful whether this compound has been obtained pure. The hydrate is readily obtained by precipitating the chloride with a caustic alkali. It dissolves readily in acids, forming *cerous salts*, which have the following reactions. *Oxalic acid* precipitates white oxalate, insoluble in excess, converted by ignition into ceroso-ceric oxide. *Acid sulphate of potassium* separates gradually a crystalline double salt, nearly insoluble in pure water, quite insoluble in a saturated solution of sulphate of potassium. *Alkaline carbonates* give a white precipitate, scarcely soluble in excess. (c) *Potash* precipitates white hydrate, insoluble in excess, converted into yellow sesquihydrate by the action of chlorine or hypochlorous acid. *Ammonia* precipitates a basic salt.

b. *Sesquioxide of Cerium. Ceric Oxide.* Ce^4O^3.—It is doubtful whether this compound has been obtained pure. The salmon-coloured powder obtained by igniting cerous oxalate or hydrate, is not pure ceric oxide, but a mixture of cerous and ceric oxides (*ceroso-ceric oxide*), not quite constant in its composition. If oxide of didymium be present, it has a red-brown colour, and dissolves in boiling hydrochloric acid. When pure it dissolves only in strong boiling sulphuric acid, forming a yellow solution, whence potash precipitates a yellow hydrate, which is readily soluble in acids, forming *ceric salts*. Their solutions are yellow, and are converted into cerous salts by boiling with hydrochloric acid. According to Bunsen (Ann. Ch. Pharm, cv. 1), when dry cerous oxalate is heated with magnesia alba, a cinnamon-brown powder is obtained, which contains all the cerium in the form of sesquioxide.

Oxide of Lanthanum, La^2O.—A white powder, obtained by igniting the hydrate or carbonate in a covered crucible: ignited in the air it turns brown, probably from the partial formation of a higher oxide. It dissolves readily in acids, even after ignition, forming *lanthanous salts:* it is also soluble in boiling chloride of ammonium. *Potash* precipitates white hydrate, completely soluble in chlorine-water, without the formation of any yellow deposit. This is the only reaction in which lanthanum differs from cerium. Lanthanous salts are colourless if quite free from didymium.

Oxide of Didymium, Di^2O.—A white powder, obtained in the same way as oxide of lanthanum. It is readily soluble in all acids, and in ammoniacal salts. *Didymium-salts* are rose-coloured, or violet: the hydrate is pale rose-colour. Their reactions closely resemble those of lanthanum-salts.

Blowpipe reactions.—All cerium compounds give with *borax* or *microcosmic salt* in the outer flame a clear bead, which is dark-red while hot, colourless on cooling: in the inner flame, a colourless bead, or, if excess of oxide of cerium be present, a yellow opaque bead. Lanthanum compounds give colourless beads. Didymium compounds give pale rose-coloured beads in the inner flame.

Separation and estimation of Cerium, Lanthanum, and Didymium.—Cerite is decomposed by boiling for some hours in strong hydrochloric acid, silica being separated. The solution is treated with ammonia, which precipitates all the metals except calcium. The precipitate is redissolved in hydrochloric acid, and oxalic acid added in excess, which gives a pale rose-coloured precipitate of oxalates of cerium, lanthanum, and didymium. By ignition this is converted into a red-brown mixture of the three oxides, from which the oxides of lanthanum and didymium may be completely dissolved by boiling for some hours with a concentrated solution of chloride of ammonium (Watts); or by treatment first with dilute, and then with strong, nitric acid (Marignac). This effects a complete separation of cerium from lanthanum and didymium. The only method for separating lanthanum from didymium is one founded on the different solubility of their sulphates: but it is not sufficiently exact for quantitative purposes.

The three metals are separated from all the metals of Group II., Subdivision A., by means of a saturated solution of sulphate of potassium. From *aluminium*, by carbonate of barium. From *glucinum* and *yttrium* by sulphate of potassium. From *zirconium* and *thorium* (only approximately) by sulphate of potassium.

Since the composition of ceroso-ceric oxide, obtained by the ignition of cerous oxalate or hydrate, is not quite constant*, cerium cannot be estimated in this form with perfect accuracy. It is better to precipitate the hydrate by potash, dissolve it in dilute sulphuric acid, evaporate to dryness, and heat the residue to commencing redness, when pure sulphate of cerium, SO^4Ce^2, is obtained. Lanthanum and didymium are estimated as oxides, obtained by igniting the hydrates or oxalates in a covered crucible.

7. **Titanium.** Ti. Atomic weight, 50.

Occurs as titanic anhydride (rutil, anatase, and Brookite): as titanate of calcium (titanite), of iron (titaniferous iron): as a compound of cyanide and nitride of titanium in bright copper-coloured crystals which are found in blast-furnaces in which titaniferous iron has been smelted. These crystals were supposed, till lately, to be metallic titanium. It is a dark-green powder, which burns very brilliantly when heated in oxygen or chlorine. It is soluble in warm hydrochloric acid.

OXIDES OF TITANIUM.—The most important oxide is

Titanic Anhydride, TiO^2.—A white powder, insoluble in water or acids (except hydrofluoric and strong sulphuric acids) obtained by the combustion of the metal in oxygen, or by igniting titanic acid.

Titanic Acid, TiO^3H^2, is obtained by precipitating a solution of the chloride, $TiCl^4$, by ammonia: it is white, insoluble in water, soluble in acids, even after drying over sulphuric acid. But titanic acid, like silicic acid, appears to exist in an insoluble, as well as a soluble, modification: for when an acid solution of titanic acid is boiled, the titanic acid is reprecipitated, and is insoluble in acids; it is converted into the soluble modification by fusion with acid sulphate of potassium. Both modifications exhibit vivid incandescence when ignited, and are converted into titanic anhydride. With an acid solution of titanic acid, *oxalic acid* gives a white precipitate: *ferrocyanide of potassium* gives a red-brown precipitate (which is green if iron is present). (c) *Gallic acid* gives an orange-red precipitate. *Alkaline sulphides* and *carbonates*, and *caustic alkalis* precipitate titanic acid, insoluble in excess: this precipitation is prevented by tartaric acid, not by chloride of ammonium. *Carbonate of barium* precipitates titanic acid completely in the cold. An acid solution of titanic acid is reduced by metallic *zinc*, *iron*, *copper*, or *tin*, a blue solution being formed, whence a violet precipitate gradually separates. A solution of titanic acid in sulphuric acid is completely precipitated by boiling: a hydrochloric acid solution only partially: the precipitation is facilitated by the addition of sulphite of sodium.

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* Bunsen (Ann. Ch. Pharm. cv. 1) states that the composition of this oxide is expressed by the formula $Ce^6O^4 = (Ce^2O + Ce^4O^3)$.

When titanic anhydride is ignited in a stream of hydrogen, it is converted into black sesquioxide, Ti^2O^3, insoluble in nitric or hydrochloric acids, soluble (to a violet solution) in sulphuric acid. (Ebelmen.)

Blowpipe reactions.—Titanic anhydride is not reduced to the metallic state when heated on charcoal with carbonate of sodium in the inner flame: this reaction distinguishes titanium from tin. With *microcosmic salt* (less easily with *borax*) titanic anhydride gives in the inner flame a bead which is violet while hot, yellowish on cooling: the colour disappears in the outer flame. If iron be present, a blood-red bead is produced. The formation of the violet colour is facilitated by the addition of metallic tin: it is more easily obtained on charcoal than on platinum-wire.

Separation and estimation of Titanium.— To obtain titanic anhydride from rutil or titaniferous iron, the mineral is finely powdered and fused with four times its weight of alkaline carbonate, and the fused mass treated with cold water, when crystalline alkaline titanate, together with ferric oxide, remains undissolved. This is dissolved in hydrochloric acid, and the solution boiled, with addition of sulphite of sodium, when the titanic acid is precipitated: or the solution is precipitated by sulphide of ammonium, and the precipitate washed with sulphurous acid, which dissolves the sulphide of iron as hyposulphate, leaving the titanic acid undissolved. Or the mineral may be fused with six times its weight of acid sulphate of potassium, and treated as above: the precipitation of titanic acid by boiling being more complete from a sulphuric acid solution. Another method is to treat the fused mass in a platinum crucible with dilute hydrofluoric acid, to purify the fluotitanate formed by re-crystallisation from hot water, and to convert it into titanate of ammonium by boiling in aqueous ammonia: on ignition, the titanate of ammonium yields titanic anhydride. Titanite is decomposed by gentle ignition with acid sulphate of ammonium.

From the metals of Group II., Subdivision A., titanium is separated by adding tartaric acid to the acid solution, and then excess of ammonia (which should produce no precipitate), and then sulphide of ammonium, which precipitates everything but the titanic acid. The filtrate is evaporated to dryness, and the residue ignited till the carbon of the organic acid is entirely burnt (which is best done in a muffle-furnace): pure titanic anhydride is left. From *aluminium* and *glucinum* titanium is separated by the precipitation of titanic acid by boiling from a sulphuric acid solution: from *yttrium* in the same way, or by carbonate of barium. From *cerium*, by sulphate of potassium. No accurate method is known for its separation from *zirconium*, which often occurs with it.

Titanium is estimated as titanic anhydride. It is precipitated by ammonia as hydrate, which, when ignited, yields titanic anhydride. A large excess of ammonia must be avoided, as some of the titanic acid would be redissolved therein.

8. **Tantalum.** Ta. Atomic weight, 137·6.

Found in a few rare minerals (tantalite, yttro-tantalite, &c.). It is a black powder, insoluble in acids, except in a mixture of nitric and hydrofluoric acids.

OXIDE OF TANTALUM. *Tantalic Anhydride*, TaO^2.—A white powder, insoluble in acids, obtained by igniting the hydrate. It can only be made soluble by fusion with potash or carbonate of potassium, when it forms tantalate of potassium, soluble in water. The hydrate, *tantalic acid*, is obtained by precipitating tantalate of potassium by hydrochloric acid, or by decomposing chloride of tantalum, $TaCl^4$, by water containing a little ammonia. It is soluble in excess of hydrochloric acid. *Carbonic anhydride*, passed through a solution of an alkaline tantalate, precipitates all the tantalum as an acid tantalate. *Sulphide of ammonium* gives no precipitate. *Chloride of barium* precipitates tantalate of barium, insoluble in water or ammoniacal salts. *Gallic acid* gives a light-yellow precipitate, soluble in alkalis. *Ferrocyanide of potassium* gives in a slightly acidulated solution, a yellow precipitate: *ferricyanide of potassium*, a white precipitate. Metallic *zinc* does not change an acidulated solution of a tantalate: but in a solution of chloride of tantalum in sulphuric or hydrochloric acid, to which a little water is added, it gives a fine blue colour, which soon disappears without changing to brown.

Blowpipe reactions.—Tantalic acid is not reduced by heating on charcoal with carbonate of sodium in the inner flame. With *borax* and *microcosmic salt* it gives in both flames colourless beads, which do not become red on addition of an iron-salt.

Separation and estimation of Tantalum.—Tantalite is analysed by fusion with six times its weight of acid sulphate of potassium: the fused mass is treated with water, which dissolves out sulphates of potassium, iron, and manganese, leaving a residue of titanic acid, stannic and tungstic acids, and ferric oxide. By digestion in sulphide of ammonium the stannic and tungstic acids are removed, and the iron converted into sulphide: the residue is filtered off, the sulphide of iron dissolved by hydrochloric acid, and the residual tantalic acid converted by ignition into tantalic anhydride.

Tantalic anhydride is distinguished from titanic anhydride, which it much resembles, by its blowpipe reactions, by its insolubility in strong sulphuric acid, and by its forming a compound insoluble in water when fused with acid sulphate of potassium. This last reaction affords the best method for separating tantalum from *titanium*, *yttrium*, *zirconium*, *manganese*, and other metals with which it frequently occurs. It is distinguished from *silicon* by its blowpipe reactions, and by the behaviour of chloride of tantalum with zinc. It is separated from silicon by volatilising the latter as fluoride. The same method serves for the separation of *titanium* from *silicon.*

Tantalum is estimated as tantalic anhydride.

9. **Niobium** or **Columbium.** Nb. Atomic weight not determined.

Occurs in a few rare minerals (columbite, Bavarian tantalite). It is a black powder, soluble in hydrochloric, hydrofluoric, and sulphuric acids, not in nitric acid. (Rose. Pogg. Ann. civ.)

OXIDES OF NIOBIUM.—Niobium forms two oxides, whose composition has not been determined, *Niobous* and *Niobic Anhydrides.* Rose has lately determined that these two oxides contain the same metal: formerly he regarded the latter as the oxide of another metal, which he called Pelopium.

Niobous Anhydride is a white powder, insoluble in acids, obtained by heating the metal in the air, or by igniting *niobous acid.* This is obtained by decomposing the chloride with water, or an alkaline niobite by hydrochloric acid. It is scarcely soluble in hydrochloric acid. A solution of an alkaline niobite, acidulated with hydrochloric or sulphuric acid, gives a red precipitate with *ferrocyanide of potassium*, bright yellow with *ferricyanide*, orange-red with *gallic acid.* *Zinc* gives a blue colour, which changes to brown.

Niobic Anhydride closely resembles tantalic anhydride. It is insoluble in all acids after ignition. From its alkaline solutions acids precipitate *niobic acid*, soluble in excess of hydrochloric acid, from which solution it is reprecipitated by sulphuric acid at boiling heat. The acidulated solution of an alkaline niobate gives a brown-red precipitate with *ferrocyanide of potassium*, white with *ferricyanide*, orange-yellow with *gallic acid.* With *zinc*, alkaline niobates and chloride of niobium behave exactly like the corresponding tantalum-compounds.

Blowpipe reactions.—With *borax* in the outer flame niobous anhydride gives a colourless bead: in the inner flame a greyish-blue bead, if sufficient anhydride be present to make the bead opaque on cooling. With *microcosmic salt* it gives in the outer flame a colourless bead: in the inner flame a violet or blue bead, the colour disappearing in the outer flame. The addition of an iron-salt produces a blood-red colour. Niobic anhydride behaves like tantalic anhydride with *borax.* With *microcosmic salt* it gives in the outer flame a colourless bead: in the inner flame a light-brown bead, tinged with violet, the colour disappearing in the outer flame, and being turned blood-red by an iron-salt.

Separation and estimation of Niobium.—The methods for the analysis of niobium compounds and for the separation of niobium from other metals, are the same as those given in the case of tantalum. No method is known for separating it from tantalum.

10. **Chromium.** Cr. Atomic weight, 26·2.

Occurs as sesquioxide (chrome-ochre): as sesquioxide combined with ferrous oxide (chrome-iron-stone): as chromate of lead, &c.

It is a greyish-white, non-magnetic metal, which does not oxidise in the air at any temperature: in the compact state it is soluble only in hydrofluoric acid.

Oxides of Chromium. *Sesquioxide*, Cr^4O^3. *Chromic anhydride*, Cr^2O^3.—There are several other oxides of chromium, *e. g.* *Protoxide*, Cr^2O, and four more intermediate between the sesquioxide and anhydride: but, as they are readily converted into one or other of the two mentioned above, it is not necessary to go into details respecting them.

a. *Sesquioxide of Chromium. Chromic Oxide.* Cr^4O^3.—A green powder, obtained by igniting the hydrate. A solution of sesquichloride of chromium is obtained by boiling a solution of bichromate of potassium, and adding hydrochloric acid and alcohol in small quantities until the solution has a deep-green colour, and ceases to evolve carbonic anhydride: from this solution ammonia precipitates sesquihydrate of chromium, of a bluish-green colour, which by ignition is converted into sesquioxide. The sesquioxide is insoluble in acids: by fusion with an alkaline carbonate and a little nitre, it is oxidised into chromic acid, which is dissolved out by water as an alkaline chromate. The hydrate is soluble in acids, forming *sesquisalts of chromium* or *chromic salts.* These salts are always coloured: there appear to be two modifications of chromic oxide, one of which forms green, the other violet, salts. Their solutions are green or violet: by transmitted light, purple-red. *Sulphide of ammonium* precipitates chromic hydrate, insoluble in excess. *Alkaline carbonates* give greenish precipitates, somewhat soluble in excess. *Carbonate of barium* precipitates the hydrate completely but slowly in the cold. *Ammonia* precipitates the hydrate, not quite insoluble in excess. *Fixed alkalis* precipitate the hydrate, readily soluble in excess to a green solution, which is reprecipitated on boiling. *Zinc* slowly reduces chromic chloride when air is excluded, a fine blue colour being produced. Soluble chromic salts are decomposed by heat.

b. *Chromic Anhydride,* Cr^2O^3.—A scarlet, crystalline solid, which is decomposed by heat, losing oxygen, and being converted into chromic oxide. It deliquesces in the air, and is very soluble in water, forming a dark-brown solution of *Chromic Acid,*

$Cr^2O^4H^2$: a dilute solution is yellow. The alkaline chromates are soluble in water, and are isomorphous with the corresponding sulphates: the normal salts are yellow, the acid salts red. The chromates of strontium, calcium, and magnesium are also soluble: all others insoluble in water, soluble in nitric acid. All chromates are coloured. Chromic acid is a powerful oxidising agent, bleaching vegetable colours, and being itself reduced to chromic oxide. All chromates are reduced by heating with strong sulphuric acid, oxygen being evolved and chromic sulphate formed ($2Cr^2O^4H^2 + 3SO^4H^2 = S^3O^{12}Cr^4 + 5OH^2 + O^3$): with strong hydrochloric acid, chlorine is evolved, and chromic chloride formed ($Cr^2O^4H^2+6ClH=Cr^2Cl^3+4OH^2+Cl^3$). Solutions of alkaline chromates are also reduced by *hydrosulphuric*, *sulphurous*, and *oxalic acids*; by *protosulphate of iron*; by *chloride of tin* on addition of hydrochloric acid; by *zinc* on addition of dilute sulphuric acid; by *alcohol*, *sugar*, and other organic compounds, in presence of free acid. The same reduction is effected by heating a solid chromate with chloride of ammonium, charcoal, or sulphur. If sufficient free acid be present, the chromic oxide formed remains in solution: if not, hydrosulphuric acid precipitates chromic hydrate mixed with sulphur. The same precipitate is produced by *sulphide of ammonium*. *Barium-salts* give with soluble chromates a yellow precipitate: *lead-salts*, a lemon-yellow, *silver-salts*, a purple-red, and *subsalts of mercury*, a brick-red, precipitate, which is converted by ignition into chromic oxide. Chromate of lead is soluble in potash. (c) A solid chromate, heated with perfectly dry chloride of sodium and fuming sulphuric acid, gives off red vapours of *chlorochromic acid*, $Cr^2O^2Cl^2$ ($Cr^2O^4H^2+2ClNa+SO^4H^2=Cr^2O^2Cl^2+SO^4Na^2+2OH^2$), which are decomposed by water into chromic and hydrochloric acids ($Cr^2O^2Cl^2+2OH^2=Cr^2O^4H^2+2ClH$). (*See* p. 26.)

Blowpipe reactions.—Chromium compounds cannot be reduced to the metallic state by heating on charcoal with carbonate of sodium in the inner flame. With *borax* and *microcosmic salts*, oxides of chromium give dark-green beads in either flame.

Separation and estimation of Chromium.—Chrome-iron-ore is analysed by fusing the finely powdered mineral in a platinum crucible with four times its weight of bisulphate of potassium: to the fused mass, when cool, twice its volume of a mixture of equal parts of nitre and carbonate of sodium is added, and the whole again fused. The whole of the chromium is thus converted into an alkaline chromate, which is dissolved out with water: the yellow solution is exactly neutralised with nitric acid, and precipitated by subnitrate of mercury; or reduced by hydrochloric acid and alcohol and precipitated by ammonia: the precipitate in either case yields on ignition pure chromic oxide. Chromate of lead is analysed by digestion with fuming hydrochloric acid and alcohol, when the chromium is dissolved as sesquichloride, while chloride of lead remains behind.

In a solution containing chromic acid, together with chromic oxide, the former may be estimated by precipitation from the *perfectly neutral* solution by subnitrate of mercury. From most of the metals of Group I. chromium is separated by hydrosulphuric acid in an acid solution. From *molybdenum*, *wolfram*, and *vanadium*, by converting the chromium entirely into chromic oxide by means of hydrochloric acid and alcohol, expelling excess of alcohol by heat, adding ammonia and sulphide of ammonium, and heating, when the chromium alone is precipitated as sesquihydrate, the other metals being converted into soluble sulpho-salts. Chromium cannot be separated from iron by means of potash: for, if the iron be in excess, some chromic hydrate remains undissolved; and if the chromium be in excess, some ferric hydrate is dissolved. Chromium is best separated from all metals of Group II., Subdivision A. (except *manganese*), by fusion with nitre and carbonate of sodium, and dissolving out the alkaline chromate with water, the other metals remaining undissolved as oxides. Another method is to treat the solution with excess of potash, and heat it with binoxide of lead, when the chromium is all converted into chromate of lead, which remains dissolved in the alkaline solution, and, after filtration, is precipitated from it by saturating the filtrate with acetic acid. (Chancel. Compt. rend. xliii. 927.) The oxidation of chromium-salts may also be effected by boiling with hypochlorite of sodium. From *manganese*, *cobalt*, *nickel*, and *zinc*, it may be separated by carbonate of barium. From *aluminium* and *glucinum* by repeated boiling with excess of potash: or better, as above, by fusion with nitre and carbonate of sodium, or by heating with potash and binoxide of lead.

Chromium is generally estimated as chromic oxide. If any chromic acid be present, it is reduced to chromic oxide by hydrochloric acid and alcohol: the chromium is then precipitated by long boiling with ammonia (avoiding excess) as hydrate, ignited, and weighed. If chromic acid only be present, it may be precipitated at once by subnitrate of mercury. Or chromic acid may be estimated directly by means of oxalic acid, which reduces it to chromic oxide, being itself converted into carbonic anhydride. If the reduction be effected in an apparatus for the estimation of carbonic acid, the carbonic anhydride may be estimated by the loss of weight, and the amount of chromic acid calculated therefrom, 3 eq. carbonic anhydride corresponding to 1 eq. chromic acid ($2Cr^2O^4H^2 + 3C^2O^4H^2 = Cr^4O^3 + 6CO^2 + 5OH^2$). For the volumetric estimation of chromic acid, *see* p. 252.

GROUP III.

Metals which are not precipitated by hydrosulphuric acid or sulphide of ammonium: but are precipitated more or less completely by normal carbonate of ammonium.

These are *barium*, *strontium*, *calcium*, and *magnesium*. They are known as the *metals of the alkaline earths*, or *alkaline-earthy metals*.

These metals decompose water, and are oxidised by moist air at the ordinary temperature. Their oxides, *the alkaline earths*, are more or less soluble in water, except that of magnesium, which is insoluble: the hydrate of magnesium is also difficultly soluble. The solutions have a powerful alkaline reaction. Their normal carbonates and phosphates are insoluble in water: hence they are precipitated from their neutral solutions by soluble normal carbonates and phosphates. Their oxides decompose chloride of ammonium either at the ordinary temperature or at boiling heat, ammonia being evolved, and the metal dissolved as chloride. Their sulphates differ in solubility: sulphate of barium is insoluble in water or dilute acids; sulphate of strontium is very slightly soluble; sulphate of calcium somewhat more soluble; sulphate of magnesium readily soluble. Since the sulphides of these metals are either soluble in, or decomposed by, water, they are not precipitated by hydrosulphuric acid under any circumstances: nor are they precipitated by sulphide of ammonium unless they are present as salts which are insoluble in water, but soluble in free acid (*e. g.* phosphates), in which case, the free acid being neutralised by the ammonia in the sulphide of ammonium, the salt is precipitated undecomposed. Under certain circumstances, therefore, these metals may appear in the sulphide of ammonium precipitate (*see* p. 198).

1. **Barium.** Ba. Atomic weight, 68·6.

Occurs chiefly as sulphate (heavy-spar), and as carbonate (witherite). It is a silver-white metal, readily soluble in acids.

OXIDE OF BARIUM. *Baryta*, Ba^2O.—A greyish friable mass, obtained by the oxidation of the metal in the air, or by ignition of the nitrate. It combines with water very readily, evolving great heat, and forming hydrate of barium, $BaHO$, which after fusion forms a white crystalline solid, readily soluble in water. The solution is known as *baryta-water:* it has a strong alkaline reaction, and readily absorbs carbonic anhydride from the air, the whole of the barium being gradually precipitated as carbonate. (C) *Sulphuric acid* or *soluble sulphates*, even the sulphates of calcium or strontium, precipitate barium completely from all its salts as sulphate, SO^4Ba^2, insoluble in water, dilute acids, or alkalis.* *Chromate* or *bichromate of potassium* precipitates yellow chromate of barium, soluble in nitric acid (distinction of barium from strontium and calcium). (C) *Fluosilicic acid* gives a white crystalline precipitate, very slightly soluble in water, insoluble in alcohol or dilute acids. *Oxalic acid* gives no precipitate, except in a very concentrated barium solution. *Phosphate of sodium* gives with neutral barium solutions a white precipitate of phosphate, PO^4Ba^2H, readily soluble in nitric, hydrochloric, or acetic acid. *Alkaline carbonates* precipitate barium completely as carbonate, CO^3Ba^2, soluble in all acids, even in carbonic acid: if carbonate of ammonia be used as the precipitant, ammonia must be added, and heat applied. *Potash* precipitates hydrate of barium, soluble in excess of water. *Ammonia* gives no precipitate. Chloride and nitrate of barium are insoluble in absolute alcohol, or in strong hydrochloric or nitric acids. Chloride of barium is the only soluble barium-salt which is not decomposed by ignition.

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* The precipitation of insoluble barium-salts, even of the sulphate, is in great measure prevented by the presence of an alkaline citrate. This is the case also with strontium and calcium, and with several of the heavy metals.—

Blowpipe reactions.—Barium compounds, when heated in the inner flame, colour the outer flame green. An alcoholic solution of a barium-salt burns with a green flame.

Separation and estimation of Barium.—Barium is separated from all the foregoing metals, except *lead*, by sulphuric acid: from *lead*, it is separated by hydrosulphuric acid.

Barium is best estimated as sulphate. It is precipitated from a dilute solution by sulphuric acid, the precipitate ignited and weighed. It may also be estimated by precipitation by carbonate of ammonium and ammonia: the carbonate is not decomposed by ignition.

2. **Strontium.** Sr. Atomic weight, 43·9.

Occurs chiefly as sulphate (celestine) and carbonate (strontianite). It is a light-yellow metal, which oxidises in the air more rapidly than calcium.

OXIDE OF STRONTIUM. *Strontia*, Sr^2O.—This compound is obtained in the same manner as baryta, which it closely resembles. It combines with water, forming a hydrate, $SrHO$, which is soluble in water, though somewhat less so than hydrate of barium. The reactions of strontium-salts closely resemble those of barium-salts. Sulphate of strontium is somewhat more soluble in water than sulphate of barium: hence *sulphuric acid* or a *soluble sulphate* does not precipitate a dilute solution of a strontium-salt so immediately as it does a barium-salt. A barium-salt gives a precipitate with a solution of sulphate of strontium, which a strontium-salt of course does not. *Bichromate of potassium* or *fluosilicic acid* do not precipitate strontium-salts. *Oxalic acid* precipitates strontium-salts more readily than it does barium-salts. *Alkalis,* and *alkaline carbonates* and *phosphates* behave with strontium-salts in the same manner as with barium-salts. Chloride of strontium is soluble, nitrate of strontium insoluble, in absolute alcohol.

Blowpipe reactions.—Strontium compounds, when heated in the inner flame, colour the outer flame carmine-red. An alcoholic solution of a strontium-salt burns with a carmine-red flame. In both cases the coloration is distinctly perceptible in presence of a considerable quantity of a barium-salt.

Separation and estimation of Strontium.—The presence of strontium is detected in a mixture of the sulphates of strontium and barium by converting them into carbonates by fusion in a platinum crucible with three parts of carbonate of sodium, converting the carbonates into chlorides by evaporating to dryness with hydrochloric acid, treating the mixed chlorides with absolute alcohol, and setting fire to the alcoholic solution of chloride of strontium. The two metals may be separated in this manner. For qualitative analysis it suffices to boil the sulphates in a strong solution of carbonate of sodium, to filter hot, and proceed as above. But a better method for the separation of strontium from *barium* is to add fluosilicic acid to the hydrochloric acid solution of the carbonates, when the barium is completely precipitated, while the strontium remains in solution. From the metals of the foregoing groups strontium is separated by hydrosulphuric acid and sulphide of ammonium.

Strontium is best estimated as carbonate, by precipitation by carbonate of ammonium and ammonia from a hot solution. The precipitation of strontium by this method is more complete than that of barium. Carbonate of strontium is not decomposed by ignition over the lamp. Strontium may also be estimated as sulphate: but, as sulphate of strontium is not absolutely insoluble in water, it is necessary to add alcohol to ensure complete precipitation, which can only be done when the original strontium-salt is soluble in alcohol.

3. **Calcium.** Ca. Atomic weight, 20.

Occurs very abundantly, chiefly as carbonate (marble, limestone, arragonite); as sulphate (anhydrite, gypsum); as phosphate (bone-earth); as chloride: and in many other salts. It is a light-yellow metal, which oxidises slowly in moist air. It decomposes water rapidly, and dilute acids still more rapidly, evolving hydrogen.

OXIDE OF CALCIUM. *Lime*, Ca^2O. — A white friable solid, obtained by igniting the carbonate. It is almost absolutely infusible. It combines with water very readily, evolving great heat, and increasing largely in volume, being converted into hydrate of calcium, $CaHO$, or *slaked lime.* The hydrate is not very soluble in water: the solution (*lime-water*) has a strong caustic taste, and an alkaline reaction. It dissolves readily in acids, forming *calcium-salts.* These closely resemble barium- and strontium-salts in their reactions. *Sulphuric acid* or *soluble sulphates* give no precipitate in very dilute solutions of calcium-salts. In concentrated solutions they precipitate slowly white sulphate of calcium, SO^4Ca^2, soluble in about 500 parts of water, more readily soluble in acids, insoluble in alcohol: hence, if sufficient alcohol be added to a calcium solution, all the calcium may be precipitated by sulphuric acid. A solution of sulphate of calcium precipitates barium- and strontium-salts, not calcium-salts. (c) *Soluble oxalates* precipitate calcium completely as oxalate, insoluble in water, oxalic and acetic acids, soluble in mineral acids: hence an acid solution of a calcium-salt must be neutralised with ammonia before adding oxalic acid. *Chromate* and *bichromate of potassium*, and *fluosilicic acid*, do not precipitate calcium-salts. *Alkalis*, and *alkaline carbonates and phosphates* behave with calcium-salts in the same manner as with barium- and strontium-salts. Chloride and nitrate of calcium are soluble in alcohol.

Blowpipe reactions. — Most calcium compounds, when heated in the inner flame, colour the outer flame yellowish-red. Alcoholic solutions of calcium-salts burn with a yellowish-red flame. Calcium cannot be detected in this way in presence of strontium.

Separation and estimation of Calcium.—For the qualitative detection of calcium in presence of barium and strontium, the solution is diluted, and the whole of the barium and strontium precipitated by dilute sulphuric acid or sulphate of potassium: the whole is then heated to boiling, filtered, the filtrate neutralised with ammonia, and oxalate of ammonium added, when the formation of a precipitate insoluble in acetic acid indicates calcium. If very little calcium be present, the precipitate does not form at once.

Calcium is separated from the metals of Groups I. and II. by hydrosulphuric acid and sulphide of ammonium. From *barium* and *strontium*, it is separated by precipitating all these metals as carbonates, by carbonate of ammonium and ammonia, dissolving the carbonates in nitric acid, evaporating to dryness, and treating the residual nitrates with absolute alcohol, which dissolves only the nitrate of calcium. The alcoholic solution is diluted with water, boiled to expel the alcohol, and precipitated by oxalate of ammonium.

Calcium is generally estimated as carbonate. The solution is neutralised by ammonia, and the calcium precipitated by oxalate of ammonium; the oxalate is converted into carbonate by ignition at a moderate heat, and weighed. If the heat be not raised above low redness, the carbonate is not at all decomposed. It is, however, safer, after the first weighing, to moisten the carbonate with a concentrated solution of carbonate of ammonium, to dry it in the water-bath, heat it gently over the lamp, and weigh it again. This method of estimating calcium cannot be applied to solutions which contain a calcium-salt which is insoluble in water, (*e. g.* phosphate,) dissolved in free acid: for the calcium-salt would be precipitated at once on neutralising the solution by ammonia. In such cases, the calcium is estimated as sulphate, being precipitated by dilute sulphuric acid, complete precipitation being insured by the addition of alcohol.

4. **Magnesium.** Mg. Atomic weight, 12.

Occurs as hydrate, carbonate, sulphate, phosphate, silicate, and other salts: it is frequently associated with calcium. It is a silver-white metal, somewhat malleable. It is not oxidised by dry air at the ordinary temperature, but when heated to redness, it burns with a brilliant flame, forming magnesia. In moist air, it becomes covered with a film of hydrate. It decomposes pure water very feebly; dilute acids with great rapidity. It seems to be intermediate in its properties between the metals of the earths proper, and those of the alkaline-earths.

OXIDE OF MAGNESIUM. *Magnesia*, Mg^2O.—A white powder, obtained by prolonged ignition of the carbonate. It is almost entirely insoluble in water, readily soluble in acids, forming *magnesium-salts.* The hydrate, MgHO, obtained by precipitating a magnesium-salt by potash, is scarcely soluble in water, readily soluble in ammoniacal salts. *Sulphuric*, *fluosilicic*, or *oxalic acid*, gives no precipitate with magnesium-salts. *Phosphate of sodium* gives no preciptiate with a dilute magnesium solution in the cold; with a concentrated solution, it precipitates phosphate, PO^4Mg^2H. (c) On adding ammonia, the whole of the magnesium is precipitated as phosphate of magnesium and ammonium, $PO^4Mg^2NH^4$, slightly soluble in pure water; insoluble in water containing ammonia, even in presence of ammoniacal salts; soluble in mineral and acetic acids. If very little magnesium be present, the precipitate forms very slowly, so that the solution must be allowed to stand for at least twelve hours in a warm place. The formation of the precipitate is facilitated by rubbing the inside of the vessel with a glass-rod. *Alkaline acid carbonates* and *carbonate of ammonium* give no precipitates in the cold. *Carbonate of potassium* or *sodium* precipitates a white basic carbonate, soluble in ammoniacal salts; the precipitate does not form in presence of ammoniacal salts. *Potash*, *soda*, *lime-* or *baryta-water*, precipitates white hydrate, insoluble in excess of water: ammoniacal salts dissolve it readily, and hinder its formation in the cold. *Ammonia* (in absence of ammoniacal salts) precipitates half the magnesium as hydrate from a *neutral* magnesium solution, the other half remaining in solution as a double salt of magnesium and ammonium, which is not decomposed by more ammonia ($SO^4Mg^2 + NH^4HO = SO^4MgNH^4 + MgHO$). Chloride of ammonium, or any ammoniacal salt, dissolves the precipitated hydrate, with evolution of ammonia ($MgHO + NH^4Cl = MgCl + NH^3 + OH^2$). If the magnesium solution contain sufficient free acid, ammonia gives no precipitate, the hydrate being dissolved in the ammoniacal salt formed. Chloride of magnesium is converted into oxide by heating with mercuric oxide, or by repeated ignition with carbonate of ammonium.

Blowpipe reactions.—Magnesium compounds do not colour the outer flame. Heated on charcoal, moistened with nitrate of cobalt, and again strongly heated, they assume a pale rose-colour: the presence of other metallic oxides interferes with this reaction.

Separation and estimation of Magnesium.—Since the hydrate and carbonate of magnesium are soluble in ammoniacal salts, it is obvious that magnesium cannot be completely precipitated by ammonia and carbonate of ammonium from a solution which, having been treated with sulphide of ammonium, must contain ammoniacal salts. It is, therefore, advisable to ensure the complete non-precipitation of magnesium by adding chloride of ammonium before precipitating the other alkaline-earthy metals by carbonate of ammonium. The filtrate from the carbonates of barium, strontium, and calcium may then contain magnesium and the alkaline metals. A portion of it is tested for magnesium by phosphate of sodium and ammonia: and if magnesium be present it must be removed before proceeding to examine for the alkalis. This is done in the following manner: the solution is evaporated to dryness and ignited to expel the ammoniacal salts; the residue is dissolved in water, baryta-water added, and the whole heated, when the magnesium is completely precipitated as hydrate. The filtrate is then freed from barium by heating with carbonate of ammonium and ammonia: the solution again evaporated to dryness, and ignited, to expel the ammoniacal salts; and the residue, which contains only the metals of the fixed alkalis, dissolved in water, and analysed as hereafter described.

Magnesium is separated from the metals of Groups I. and II. by hydrosulphuric acid and sulphide of ammonium. From *barium*, *strontium*, and *calcium*, by carbonate of ammonium in presence of ammoniacal salts: or from *barium* and *strontium* by sulphuric acid, and from *calcium*, by oxalate of ammonium in presence of chloride of ammonium.

Magnesium is generally estimated as pyrophosphate, $P^2O^7Mg^4$. It is precipitated by phosphate of sodium and ammonia, as phosphate of magnesium and ammonium, which is washed with dilute ammonia, dried, and ignited, when it is converted into pyrophosphate ($2\,PO^4Mg^2NH^4 = P^2O^7Mg^4 + 2NH^3 + OH^2$). If no other fixed substance be present, magnesium may be estimated as sulphate, by evaporating to dryness, moistening the ignited residue with slightly diluted sulphuric acid, and expelling the excess of the acid at a low red heat.

GROUP IV.

Metals of the alkalis, or Alkaline metals.

Potassium, Sodium, Lithium, Ammonium.

These metals are lighter than water. They decompose water violently at the ordinary temperature, evolving hydrogen, and forming a solution of an alkaline hydrate, which has a caustic taste, and a powerful alkaline reaction. The compounds of these metals with *chlorine*, *bromine*, *iodine*, *fluorine*, *cyanogen*, and *sulphur* are soluble in water: as are nearly all the rest of their salts. The sulphates of potassium and sodium are completely converted into chlorides by repeated ignition with chloride of ammonium.

1. **Potassium**, or **Kalium**. K. Atomic weight, 39.

Occurs abundantly as nitrate (saltpetre or nitre); as sulphate (in alum); as silicate (in various minerals); also in mineral springs, and in the ashes of plants. It is a white metal, which oxidises with great rapidity in moist air, so that it is necessary to preserve it from contact with the air by keeping it immersed in some liquid on which it exercises no decomposing action: petroleum or rock-oil is generally employed for this purpose. It decomposes water with extraordinary violence, evolving so much heat that the liberated hydrogen is set on fire, and burns with a violet flame. It is volatile at a red heat.

OXIDE OF POTASSIUM. K^2O. — A grey solid mass, obtained by heating potassium with hydrate of potassium in the proper atomic proportion. It combines readily with water, forming the hydrate, KHO (potash), which is a white, hard, brittle substance, that deliquesces in moist air, and is very readily soluble in water, (forming *solution of potash*), and in acids, (forming *potassium-salts*). (c) With *bichloride of platinum*, potassium solutions, if not too dilute, give a yellow crystalline precipitate of chloroplatinate of potassium, $PtCl^3K$, slightly soluble in water, insoluble in alcohol and in acids. If very little potassium be present, the solution must be saturated with hydrochloric acid, bichloride of platinum added, the whole evaporated to dryness, and the residue treated with alcohol, which leaves the chloroplatinate undissolved. (c) Concentrated potassium solutions are precipitated by *acid tartrate of sodium*, as acid tartrate of potassium, $C^4H^4O^6KH$; it is white; crystalline, soluble in about 180 parts cold water, readily soluble in mineral acids or in alkaline solutions. The formation of the precipitate is facilitated by agitating the solution. *Fluosilicic acid* gives a white gelatinous precipitate of fluosilicate of potassium. *Perchloric acid* gives a precipitate of perchlorate, insoluble in alcohol. When a concentrated solution of *sulphate of aluminium* is added to a concentrated solution of a potassium-salt, octahedral crystals of alum are deposited on evaporating the solution (p. 164). Normal sulphate, carbonate, phosphate, arsenate, and borate of potassium are not decomposed by heat. The chloride, bromide, and iodide are volatile without decomposition at a very strong heat. Most other potassium-salts are decomposed by heat.

Blowpipe reactions. — Potassium compounds impart a violet colour to the outer flame. Alcoholic solutions of potassium-salts burn with a violet flame. The colour is not perceptible to the naked eye in presence of sodium (or lithium): but if a thick piece of dark-blue glass be interposed between the eye and the flame, the yellow sodium-flame is completely cut off, and the potassium-flame is distinctly visible, of a rich reddish-violet colour. In this manner a very small amount of potassium may be detected in presence of a large quantity of sodium (Cartmell).

Separation and estimation of Potassium.—Potassium is separated from all the foregoing metals by hydrosulphuric acid, sulphide and carbonate of ammonium. It is estimated as chloroplatinate: alcohol is added to complete the precipitation, the precipitate is washed with alcohol, dried at 100°, and weighed.

Potassium, when it occurs in a compound not containing any other metal, is estimated as sulphate or chloride. Any potassium-salt of a volatile acid is converted into sulphate by heating with sulphuric acid, excess of sulphuric acid is expelled by heat, and the residual sulphate weighed. The expulsion of the last traces of sulphuric acid is facilitated by dropping a fragment of carbonate of ammonium into the crucible. In estimating potassium as chloride, ignition must be performed in a covered crucible, the chloride being somewhat volatile at a strong heat.

2. **Sodium**, or **Natrium.** Na. Atomic weight, 23.

Occurs, like potassium, as carbonate, nitrate (Chili saltpetre), &c.: abundantly as chloride, both solid (rock-salt) and in solution in sea-water. It much resembles potassium in appearance and properties, and requires the same precautions for its preservation. It does not however combine with oxygen quite so violently: when it decomposes water the heat evolved is sufficient to fuse the sodium, but not generally to inflame the liberated hydrogen.

OXIDE OF SODIUM. Na^2O.—Prepared in the same way as oxide of potassium, which it most closely resembles. There is the same resemblance in external appearance, solubility, &c. between the hydrate of sodium (soda), and potash. Sodium-salts are even more generally soluble than potassium-salts: they give no precipitates with *bichloride of platinum*, *tartaric* or *perchloric acid*, and no crystals of alum with *sulphate of aluminium*. *Fluosilicic acid* gives a gelatinous precipitate in concentrated solutions. *Metantimonate of potassium* (p. 91) gives (in dilute solutions only after some time) a white precipitate of metantimonate of sodium. The sodium solution must be neutral or slightly alkaline, for free acid would separate antimonic acid from the reagent. This reaction detects sodium in presence of the other alkaline metals: but no other metals must be present in the solution. When ignited, sodium-salts behave like potassium-salts: chloride of sodium is less volatile than chloride of potassium.

Blowpipe reactions.— (c) Sodium compounds impart an intense yellow colour to the outer flame, which quite conceals the coloration produced by any other metal. Alcoholic solutions of sodium-salts burn with a yellow flame.

Separation and estimation of Sodium.— Sodium is separated from all the metals of Groups I., II., and III. by hydrosulphuric acid, sulphide of ammonium, and carbonate of barium. From *potassium* by bichloride of platinum and alcohol. This separation is best effected when the metals are in the form of chlorides. The amount of potassium being determined from the weight of the chloroplatinate, that of sodium may frequently be estimated by difference. To estimate the sodium directly, the filtrate from the potassium-salt must be evaporated to dryness at a very gentle heat, and the residue ignited in a platinum crucible till the chloroplatinate of sodium and the excess of platinic chloride are entirely decomposed: this decomposition is facilitated by the addition of a few crystals of pure oxalic acid during ignition. The chloride of sodium thus formed is dissolved out with water, evaporated to dryness, ignited, and weighed. Removing the platinum by hydrosulphuric acid does not answer (Rose).

Sodium is estimated as sulphate or chloride. The process is the same as that given for potassium.

3. **Lithium.** Li. Atomic weight, 6·5.

Occurs, not very abundantly, in certain minerals (lepidolite, petalite, spodumen, triphylline, amblygonite). It is a white metal, much harder than potassium or sodium. It is lighter than any known solid or liquid. It is not oxidised in dry air; in moist air it tarnishes slowly: when heated in air it combines with oxygen, burning with a dazzling white flame. It decomposes water at the ordinary temperature; but less violently than potassium or sodium.

OXIDE OF LITHIUM. Li^2O.—A white solid substance, obtained by burning the metal in dry oxygen, or decomposing the nitrate by prolonged heat. It deliquesces in the air, but less rapidly than potash or soda: it is slowly soluble in water. The hydrate, LiHO (lithia), is a white sium and sodium: the solution is strongly alkaline. Most lithium-salts are deliquescent; all are soluble in water: the carbonate and phosphate are difficultly soluble, hence *carbonate* or *phosphate of sodium* gives a white precipitate with concentrated solutions of lithium-salts, especially on boiling. In presence of sufficient ammoniacal salt, carbonate of sodium gives no precipitate. Lithium-salts are not precipitated by *bichloride of platinum, tartaric* or *perchloric acids*, or *metantimonate of potassium:* they form no double compound with *sulphate of aluminium.* They are generally more easily decomposed by heat than the salts of potassium and sodium: the volatility of the chloride is between that of chloride of potassium and chloride of sodium. Chloride of lithium is soluble in a mixture of absolute alcohol and ether.

Blowpipe reactions.—Lithium compounds impart a crimson colour to the outer flame, which has less yellow in it than the strontium-colour. Alcoholic solutions of lithium-salts burn with a crimson flame. Heated on platinum-foil with carbonate of sodium in the inner flame, they attack the platinum, producing a brown stain: the fused mass is transparent while hot.

Separation and estimation of Lithium.—The most abundant lithium-ore is lepidolite. The following method of extracting lithium from it is given by Troost (Ann. Ch. Phys. [3.] li. 121):—10 parts of the powdered mineral are heated in a furnace with 10 parts carbonate of barium, 5 parts sulphate of barium, and 3 parts sulphate of potassium. When the fused mass is cold, the crucible is broken, when a transparent glass is found at the bottom, and a white crystalline solid at the top, consisting of sulphates of barium, lithium, potassium, and sodium. The alkaline sulphates are dissolved out by water, converted into chlorides by chloride of barium, the potassium separated by bichloride of platinum, and the chlorides of lithium and sodium by alcohol and ether. In operating on a large scale, the double sulphate of lithium and potassium is separated by fractional crystallisation. By increasing the proportion of sulphate of potassium, the same method is applicable to petalite. The richest lithium-ore is triphylline, a phosphate of iron, manganese, and lithium. Müller gives the following method for extracting lithium from it. The coarsely powdered mineral is dissolved in strong hydrochloric acid, nitric acid being added to peroxidise the iron: the solution is then evaporated to dryness, and treated with water, when all the iron remains as insoluble phosphate. The solution, containing chlorides of lithium and manganese, and a little phosphoric acid, is treated with sulphide of barium, which removes the two latter substances; the excess of barium is removed by sulphuric acid (or carbonate of ammonium), and the filtrate evaporated to dryness and ignited. The chloride of lithium thus obtained frequently contains chloride of sodium, which may be separated by alcohol and ether. (Ann. Ch. Phys. [3.] xlv. 350.)

Lithium is separated from *potassium* by bichloride of platinum: from *sodium* by the solubility of its chloride in alcohol and ether.

Lithium may be estimated as sulphate or chloride.

4. **Ammonium.** NH^4. Am. Atomic weight, 18.

This is a hypothetical metal, supposed to exist in ammoniacal salts. It has never been isolated; but an amalgam of it with mercury is prepared without difficulty.

Ammonia, NH^3, is a compound of very frequent occurrence in atmospheric air, soils of all kinds, and in the juices of plants. It is very easily obtained by heating chloride of ammonium (sal-ammoniac) with quick-lime. At the ordinary temperature it is a colourless gas, possessing an alkaline reaction: it is very soluble in water with evolution of heat, producing a colourless, powerfully alkaline solution of *hydrate of ammonium* ($NH^3 + H^2O = NH^4HO$), analogous to hydrate of potassium, KHO. This solution neutralises acids completely, forming *ammonium-salts*, in which NH^4 plays the part of a metal, (*e. g.* $ClNH^4$, $SO^4(NH^4)^2$ analogous to ClK, SO^4K^2). Ammonium-salts are strictly isomorphous with potassium-salts. (c) All ammonium-salts are decomposed when heated with a fixed alkali or an alkaline earth, gaseous ammonia being evolved, which is easily recognised by its characteristic smell, by its restoring the blue colour to reddened litmus-paper, and by its forming dense white fumes of chloride of ammonium on contact with a glass-rod moistened with dilute hydrochloric acid. If only a very small trace of an ammonium-salt be present, it is readily detected by heating the solution with caustic lime in a test-tube, in the mouth of which is placed a strip of paper moistened with a dilute neutral solution of *subnitrate of mercury*, *sulphate of copper*, or *sulphate of manganese*: in the first case a black stain is formed on the paper, in the second a blue, in the third a brown. *Subnitrate of mercury* gives a brown colour in solutions containing free ammonia. A slightly alkaline solution of an ammonium-salt gives a white precipitate with *chloride of mercury*. (c) A solution of *molybdate of sodium* containing *phosphoric acid* gives with ammonium solutions a yellow precipitate, soluble in alkalis and non-volatile organic acids. In very dilute solutions the precipitate does not form immediately. (c) When a solution containing free ammonia or an ammonium-salt is mixed with *potash*, and *a solution of iodide of mercury in iodide of potassium* added, a brown precipitate or coloration is immediately produced. (Nessler). This is by far the most delicate test for ammonia. With *bichloride of platinum* and *acid tartrate of sodium* ammonium-salts behave precisely like potassium-salts. The chloroplatinate of ammonium, $PtCl^3NH^4$, is converted by ignition into metallic platinum, perfectly free from chlorine. The carbonaceous residue left on igniting the acid tartrate of ammonium has no alkaline reaction. Ammonium-salts of fixed acids lose their ammonia when ignited: all others are volatilised by heat, some being decomposed (sulphate, nitrate, &c.), others without decomposition (chloride, iodide). Nitrate of ammonium, or any ammonium-salt mixed with sufficient nitre, is entirely decomposed and volatilised at a very low heat. Alcoholic solutions of ammonium-salts burn with a blue or violet flame.

Separation and estimation of Ammonium.—In qualitative analysis, ammonium is always tested for in a separate portion of the substance under examination. Ammonium is separated from all other metals by the decomposition of its salts when heated with caustic lime. The ammonia evolved is led into hydrochloric acid, and the resulting solution of chloride of ammonium precipitated by bichloride of platinum and alcohol.

Ammonium is estimated as chloroplatinate. It is precipitated by bichloride of platinum and alcohol; the precipitate is converted into metallic platinum by ignition, and weighed: the amount of ammonium is calculated from the weight of the platinum. The chloroplatinate may also be collected on a weighed filter, dried at 100°, and weighed as such.

PART III.

COURSE OF QUALITATIVE ANALYSIS.

I. Preliminary examination and solution of solid bodies.

The first thing to be done in the qualitative analysis of a solid body is to obtain some general information as to its nature and composition. This information, which must necessarily precede any more special analysis by the wet way, is obtained partly by an accurate observation of the physical properties of the substance (its form, colour, lustre, hardness, specific gravity, &c.): but chiefly by chemical examination *in the dry way; i. e.* by observing the behaviour of the substance *at a high temperature*, either alone, in contact with air, or with some chemical compound which produces either decomposition or simple solution.

If the substance contain organic matter, it usually blackens when heated, and evolves carbonic anhydride when heated with sulphuric acid and bichromate of potassium. In this case it is best to remove the organic matter before proceeding further: since its presence materially interferes with the reactions of many mineral compounds. This may generally be effected by heating the substance strongly for some time in contact with air (more speedily with oxygen), until the whole of the carbon is converted into carbonic anhydride. In many cases, the oxidation of the carbon is facilitated by dropping nitric acid upon the heated substance. The preliminary examination of mineral or inorganic substances by the dry way is conducted according to Tables I. and II.: by which we can ascertain not only the general chemical nature of the substance, but also the presence or absence of many metals, and of some non-metallic elements. Table IX. serves exclusively for the preliminary examination for *acids;* especially for such acids as are volatile, or as yield volatile products of decomposition when heated with concentrated sulphuric acid. These tables require no explanation: their constant practical use can alone give the necessary accuracy to the information obtained by their means.

After having ascertained by the preliminary examination in the dry way to what class of bodies the substance under examination belongs, the next step is to bring it into the only form which is fitted for its qualitative analysis in the wet way, *i. e.*, into the liquid state — in other words, to *dissolve* it. In order to effect this, it is generally necessary (when the nature of the substance allows it) to reduce it to a fine powder, by pounding in a mortar, and, if necessary, by subsequent *levigation* with water. This is indispensable in the case of minerals, especially of silicates, and of all other difficultly soluble, insoluble, or difficultly decomposable compounds. The finely-powdered substance is then boiled with *water*, in order to ascertain its complete or partial solubility or insolubility therein. If it be not completely dissolved, the solution is filtered off from the residue, and a drop or two of it evaporated to dryness on platinum-foil. when, if the substance is partially soluble in water, a distinct residue is left; if the substance is completely insoluble, there is no residue. In the former case the aqueous solution is tested with litmus-paper, to see whether it has a *neutral*, *acid*, or *alkaline* reaction; and set aside for further examination. The portion insoluble in water is then treated successively with *dilute* and *concentrated hydrochloric acid*, particular attention being paid to the nature of the gas, if any, thereby evolved. *Carbonates* evolve carbonic anhydride with effervescence: *peroxides* and *chromates* evolve chlorine: *cyanides*, hydrocyanic acid: many *sulphides*, hydrosulphuric acid: *sulphites* and *hyposulphites*, sulphurous anhydride, with separation of sulphur in the latter case: most *metals* (zinc, iron, tin, &c.) evolve hydrogen; or, if arsenic or antimony be present, arsenide or antimonide of hydrogen. If hydrochloric acid does not completely dissolve the substance, it generally effects the complete separation of one or more elements; for which reason the solution should be separated from the residue, and examined apart. The portion insoluble in hydrochloric acid is then treated successively with *nitric acid* and *aqua-regia.* Most *sulphides,* thus treated, leave a residue of sulphur, which, on prolonged digestion with the acid, collects into yellow globules which swim on the surface of the liquid; or disappears altogether, being oxidised into sulphuric acid, which may be detected in the solution, unless it forms an insoluble salt with the dissolved metal. Thus *sulphide of lead* leaves a white residue of *sulphate of lead,* when treated with nitric acid: *sulphides of antimony* and *tin* are converted into white *oxides: sulphide of mercury* is insoluble in nitric acid, readily soluble in aqua-regia.

Most metals are completely soluble in nitric acid: the only metals not attacked by it are *gold, platinum, iridium,* and the rarer metals found in platinum-ores. *Gold* and *platinum* are soluble in aqua-regia: *tin* and *antimony* are not dissolved by nitric acid, but are converted into white oxides, insoluble in excess of the acid; they are readily soluble in aqua-regia (or hydrochloric acid and chlorate of potassium) provided excess of nitric acid be avoided.

If the substance be not dissolved or decomposed by the above acids, after long digestion at a gentle heat, it must be one of the bodies mentioned in Table III.: and it must be rendered soluble by one of the methods indicated in that table, the particular method chosen depending upon the general chemical nature of the substance, to be ascertained by an examination in the dry way, according to Tables I. and II.

II. Qualitative analysis of solutions.

In the qualitative analysis of solutions there are two preliminary steps which should always be taken, before proceeding to the regular course of analysis in the wet way by Tables IV.—VIII. These are, 1. To ascertain whether the solution contains any non-volatile constituents. This is done by evaporating a small portion of it to dryness on platinum-foil: if a fixed residue remains, which does not volatilise when strongly heated, some *non-volatile* compounds are present: if there be no fixed residue, the solution contains only *volatile* constituents. In the former case the residue should be examined by Tables I. and II. 2. To ascertain whether the solution is neutral, acid, or alkaline to test-paper.

These preliminaries are of course unnecessary when the solution has been made by the student himself, as described in the foregoing section; but they should never be neglected with a solution given for examination, since, if carefully performed, they may enable him to conclude at once as to the presence or absence of whole groups of bodies. Thus it is evident that a solution which, after *careful* evaporation (not rapid boiling), leaves no residue, can contain no non-volatile metallic salts. A *neutral* solution in general can contain only salts of the alkaline and alkaline-earthy metals, since the salts of almost all the other metals have an *acid* reaction. An *alkaline* solution (in which no non-volatile organic compounds are present) cannot contain any of the metals whose oxides are insoluble in alkaline liquids: if the alkaline reaction be caused by the presence of an alkaline carbonate, the presence of the alkaline-earthy metals is impossible. (There are, however, exceptions to this rule: an alkaline solution may contain salts of copper and sesquisalts of iron, if any non-volatile organic compound be present; it may also contain such oxides, cyanides, and sulphides as are soluble in cyanide of potassium and alkaline sulphides.) The presence of certain acids implies the absence of certain metals, and *vice versâ:* the same acid solution cannot contain sulphuric acid and barium, hydrochloric acid and silver, &c. Silver need not be looked for in an alloy soluble in hydrochloric acid: nor gold, antimony, tin, &c., in one soluble in nitric acid.

It is generally advisable to examine for acids and metals in separate portions of the solution.

a. Examination for metals.

Table IV., which exhibits in a compendious form the behaviour of all the metals to *general* reagents, gives a general outline of the course to be adopted in examining a solution for metals. With a very little reflection, the table will be perfectly intelligible. The following rules, however, of the utmost importance in the analysis of mixtures which may contain any number of constituents, must always be kept in mind.

1. *The precipitation by each general reagent must be complete.*—To ensure this, the reagent must be added gradually, allowing the precipitate already formed to subside between each addition, until no further precipitate is produced. In the case of hydrosulphuric acid, the precipitation is complete when the solution, *after being agitated*, still smells strongly of the gas. Gentle heating facilitates the separation of precipitates in almost every case. Arsenic (as arsenic acid), molybdenum, platinum, iridium, and rhodium, are very slowly precipitated by hydrosulphuric acid, the solution requiring to be left in a warm place for from 12 to 24 hours after its complete saturation with the gas. Pentasulphide of arsenic separates much more quickly when the solution is heated to 60° or 70°.

2. *Each group, when precipitated, must be thoroughly freed by washing with water from all members of the subsequent groups which may be contained in the solution.*—This washing is effected, according to circumstances, either on a filter, or by *decantation*, *i.e.* by allowing the precipitate to subside, pouring off the clear liquid, shaking up the precipitate with water, and repeating the operation as often as is necessary. If the precipitate contains any easily oxidable sulphides, a little hydrosulphuric acid must be added to the wash-water (if the sulphide is insoluble in dilute acids, *e.g.* sulphide of copper), or a little sulphide of ammonium (if the sulphide is soluble in dilute acids, *e.g.* sulphides of iron and manganese), in order to prevent the partial oxidation of the sulphide by exposure to the air during the washing of the precipitate. After the precipitation of each group, it is advisable to ascertain the presence or absence of any members of the succeeding groups, by carefully evaporating on platinum-foil a moderate quantity of the filtrate: if, after ignition, there is no distinctly visible residue, non-volatile substances need not be looked for further.

tion and *thorough washing*) be neglected, metals belonging to one group are liable to be found among those of another group; and consequently, as the analysis proceeds, reactions will be obtained which are not mentioned in the tables of the different groups, and which will be the source of great perplexity to the student.

3. *The mineral acid employed to acidify the original solution* (when it is not already sufficiently acid) *is either hydrochloric or nitric acid.*—It is generally employed dilute, and not in sufficient quantity to interfere with the formation of those sulphides which are insoluble in dilute acids. Hydrochloric is generally preferable to nitric acid: and attention must then be paid to the possible precipitation (of chlorides of silver and lead, and subchloride of mercury) mentioned in Table IV.

4. *The application of confirmatory tests must never be neglected.*—When, in the course of a systematic qualitative analysis, one or more members of the different groups have been recognised as constituents of the substance examined, by means of the reactions given in the tables, the analyst (especially the beginner) should proceed to apply a series of confirmatory tests, either to the original substance or to each constituent that he has separated from it, in order to control the results already obtained. The beginner should never neglect these confirmatory tests; since the object of analytical practice is not only to acquire the simple course of analysis, but also to become familiar with the reactions of bodies generally. The observance of this important rule is the only means by which the unpractised student can avoid errors in his analysis: for these errors arise invariably either from ignorance of the reactions of bodies generally, or from neglect of the conditions on which depends the appearance of those phenomena which we regard as proofs of the presence of different bodies. It is for this reason that the reactions of acids and metals are given in the first and second parts of this work in such detail, that no difficulty can be experienced in the selection of any reasonable number of confirmatory tests.

The further distinction and separation from each other of the metals constituting each group, are effected according to Tables

V. VI. VII. and VIII. Table V. includes those metals which are precipitated by hydrosulphuric acid from an acid solution: Table VI. those which are precipitated by sulphide of ammonium: Table VII. those which are precipitated by carbonate of ammonium: Table VIII. *magnesium* and the *alkaline metals.*

In connection with Group II. (Table VI.) it is to be observed that under certain circumstances the metals of Group III. (the alkaline-earthy metals) may appear in the sulphide of ammonium precipitate. Those salts of barium, strontium, and calcium which are soluble in water, are not precipitated by ammonia or sulphide of ammonium; neither are magnesium-salts in presence of a sufficient quantity of ammoniacal salt. But there are some salts of these metals which, though insoluble in water, are soluble in acids: and if any of these salts are present in the acid solution, they will of course be precipitated unchanged when the acid that holds them in solution is neutralised by the addition of ammonia, or (what comes to the same thing) of sulphide of ammonium. The alkaline-earthy salts which may thus appear in the sulphide of ammonium precipitate are phosphate of magnesium; phosphate, oxalate, borate, fluoride, of calcium, strontium, or barium; as well as the salts of several other non-volatile organic acids. These salts are insoluble in potash, and resemble the earths in their behaviour with general reagents. If an *oxalate* be present, the precipitate after ignition effervesces when dissolved in hydrochloric acid: the solution is not precipitated by ammonia, and should be examined for the alkaline-earthy metals in the usual manner. Alkaline-earthy *phosphates* are not decomposed by ignition: the metal they contain is ascertained by dissolving them in as little hydrochloric acid as possible, adding acetate of sodium to the solution, and then sesquichloride of iron, drop by drop, until a red colour is produced. The solution is then heated to boiling and filtered: the residue contains all the phosphoric acid as basic phosphate of iron, and the filtrate contains the alkaline-earthy metals as chlorides, to be sought for in the usual way. But the best method is to dissolve the precipitate in hydrochloric acid, and to test for each of the acids and metals successively in separate portions of the solution, as described in the latter part of

Table VI. *Hydrofluoric acid* must be sought for in the original substance.

β. *Examination for acids.*

The qualitative examination for acids is on the whole more difficult than that for metals: still, with due care, it may be executed with great precision. In almost every case the preliminary examination by Tables I. and IX., as well as the nature of the metals already found, give information as to what class of acids should especially be looked for. The knowledge of the solubility of different salts, and of the reactions of their aqueous solutions with vegetable colours, is of the greatest importance in this examination. By heating the substance either alone or with concentrated sulphuric acid (Table IX.), the presence or absence of *organic* and of *volatile inorganic* acids is at once ascertained. Whenever there is reason to expect the presence of several acids or their salts in the substance under examination, attention must be paid to the causes of error which are likely to arise in the preliminary examination from the fact that the behaviour of a mixture of salts, when heated alone or with sulphuric acid, is often different from that of each individual salt under the same circumstances. Thus a mixture of a nitrate or chlorate with a salt of an organic acid does not blacken when ignited, but commonly detonates; and if the organic compound be present in sufficient quantity, no trace of a nitrate is found after ignition, but only a carbonate, provided the base be an alkaline or alkaline-earthy metal. When heated with concentrated sulphuric acid, a mixture of a chloride and a nitrate does not evolve hydrochloric and nitric acids, but chlorine and red nitrous fumes: in a mixture of a sulphite and a nitrate (chlorate, chromate, &c.), the sulphurous acid is converted into sulphuric acid; in a mixture of a sulphide and a sulphite, the two acids decompose each other, sulphur being separated, and the characteristic smell of each destroyed.

In order not to overlook the presence of uncombined volatile organic acids, the acid solution is neutralised with carbonate of sodium, evaporated to dryness, and ignited: when the organic acid, which, if free, would have been volatilised undecomposed, is decomposed with separation of carbon.

For the detection of the most important acids in a solution in the wet way, the usual course is that laid down in Tables X. and XI. The employment of *general* reagents in examining for acids has, in most cases, no other aim than to ascertain the presence or absence of one or more members of each group of acids: the detection of each several acid belonging to these groups requires the further employment of the *special* reagents which are indicated in the tables.

When, as is frequently the case, a neutral solution is required in testing for acids, the solution, if acid, is neutralised by ammonia, if alkaline by nitric acid, or, if nitrate of silver is not used as a reagent, by hydrochloric acid. If, however, the substance to be examined is insoluble in water, but soluble in acids without apparent decomposition (*e. g.* an alkaline-earthy phosphate or oxalate), it is obvious that the acid solution cannot be neutralised by ammonia, since the salt would thereby be precipitated unchanged. In many such cases (of which we have already seen instances in the sulphide of ammonium precipitate) the substance may be dissolved in acetic acid, and the acid solution tested for oxalic acid by chloride of calcium, for phosphoric acid by sesquichloride of iron, &c. But the most universal method of obviating this difficulty is to remove all the metals except those of the alkalis before commencing the examination for acids. The volatile acids may be separated from all fixed acids and bases by distillation with dilute sulphuric acid. In analysing an insoluble salt of an organic acid, the acid is removed by boiling the compound with carbonate of sodium, and detected in the filtrate after neutralisation with hydrochloric acid. When a solution containing hydrosulphuric acid or a soluble sulphide has to be tested for such acids as are precipitated by nitrate of silver from an acid solution, but not by ferric salts (*e. g.* hydrochloric, hydrobromic, hydriodic acids), the hydrosulphuric acid is removed by adding ferric sulphate, and the filtrate, acidulated with nitric acid, tested with nitrate of silver. Compounds insoluble in water and acids are rendered soluble by the methods given in Tables III. and XI. and then examined for acids in the wet way.

We have said that the volatile acids may be at once separated from a solution by distillation with dilute sulphuric acid. It is often advisable to employ this process, for which the following hints, relating to the acids of most frequent occurrence, will be found useful. The distillation should be effected in a small tubulated retort, so arranged that all the gas evolved is conducted into lime- or baryta-water. If gas is given off immediately on adding sulphuric acid, before applying heat, *carbonic*, *sulphurous*, or *hydrosulphuric* acid is present: they may be distinguished by the smell. If carbonic anhydride is evolved after *heating for some time*, *oxalic acid* is present. Continue to heat gently, not to boiling, and collect the distillate in three separate portions:

Examine portion 1 for *hydrocyanic*, *hydrochloric* (perhaps *acetic* and *formic*) acids:
Examine portion 2 for *hydrochloric*, *hydrobromic*, *hydriodic**, *acetic*, *formic*, and *nitric* acids:
Examine portion 3 for *nitric*, *succinic*, and *benzoic* acids.

When the third distillate has been collected, and the sulphuric acid in the retort has become concentrated, heat strongly: the evolution of carbonic anhydride and blackening indicates the presence of non-volatile organic acids (*e. g. tartaric*, *citric*). Empty the retort into a porcelain basin, neutralise with ammonia, evaporate to dryness, and ignite: blackening indicates non-volatile organic acids. Watch for the peculiar smell of *tartaric* acid. Exhaust the ignited residue with water, and examine the solution for *phosphoric* acid. It is to be noted that sulphurous acid may appear in the distillate when it did not exist in the original solution, owing to the deoxidation of the sulphuric acid. The distillate should also always be tested for sulphuric acid, which is not unfrequently carried over mechanically if the distillation be performed too rapidly.

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* The formation of violet vapours in the retort towards the end of the distillation indicates the presence of *hydriodic acid.*

PART IV.

EXAMPLES FOR QUANTITATIVE ANALYSIS.

Section I. Analysis by weight.

1. **Sulphate of Copper.** $SO^4Cu^2 + 5H^2O$.

For the analysis of this salt, it is necessary to determine separately the *water*, the *copper*, and the *sulphur and oxygen.* It is generally advisable (though not always necessary) to take separate portions of the salt for the determination of the metallic and non-metallic elements: $\frac{1}{2}$ grm. is generally sufficient. The salt should be purified by re-crystallisation before analysis.

a. *Water.*—A weighed portion of the salt, finely powdered, and dried over sulphuric acid, is heated to about 200°, till it is quite white, and ceases to lose weight: the weight lost consists of water.

b. *Copper.*—The same portion of the salt is dissolved in water, heated to boiling, and precipitated while hot by caustic potash, which should not be added in great excess. The precipitated cupric oxide is collected on a filter, washed with hot water till the washings leave no residue when evaporated on platinum-foil, and ignited in a platinum crucible, together with the ashes of the filter.* As some of the oxide may have been reduced by the carbonaceous matter of the filter, it is moistened with a few drops of nitric acid, again ignited in the covered crucible, and weighed when cool. As cupric oxide rapidly absorbs moisture from the air, the crucible should be allowed to cool over sulphuric acid, and weighed (still covered) as quickly as possible. (Cu^2O : : Cu^2 : 79·4 : 63·4.)

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* The best method of incinerating a filter is (after the precipitate has been removed from it as completely as possible) to twist it in a coil of platinum-wire, set it on fire, and hold it so that the ashes shall drop into the crucible. In all cases when the filter ash is ignited with the precipitate, the weight of the ash must be deducted: this is ascertained by incinerating six filters of the same size with that employed, and taking the sixth part of the weight of their ashes as the average weight of the ash of a filter of that size.

c. *Sulphur and Oxygen*—A fresh portion of the salt dissolved in water (or the filtrate from the cupric oxide) is acidulated with hydrochloric acid, and completely precipitated by chloride of barium : the whole is then warmed for some minutes, and the precipitate allowed to subside. The clear liquid is then poured on the filter, the precipitate stirred up with hot water, and not thrown on the filter till it has completely subsided. If these precautions be not attended to, the precipitate will pass through the filter. The sulphate of barium is washed thoroughly, dried, ignited, and weighed with the incinerated filter. (SO^4Ba^2 : SO^4 : : 233·2 : 96.)

Calculated percentage.

Hydrated salt,	SO^4 38·49	Cu^2 25·42	$5H^2O$ 36·09.
Dry „	SO^4 60·226	Cu^2 39·774	

2. **Sulphate of Iron.** $SO^4Fe^2 + 7 H^2O$.

a. *Iron.*—A weighed portion of the salt (which must be free from sesquisalt) is dissolved in water, the solution boiled with aqua-regia till the whole of the iron is converted into sesquisalt, and precipitated with excess of ammonia. The precipitated ferric hydrate is collected on a filter, washed, dried, ignited with the filter, and weighed. (Fe^4O^3 : Fe^4 : : 10 : 7.)

b. *Sulphur and Oxygen.*—Estimated as in 1.

c. *Water.*—The salt loses six atoms of water when heated to about 100°; the seventh it does not part with below 280°, near which temperature it is decomposed.

Calculated percentage.

Hydrated salt,	SO^4 34·532	Fe^2 20·144	$7H^2O$ 45·324.
Dry „	SO^4 63·16	Fe^2 36·84.	

3. **Chloride of Sodium.** ClNa.

Common salt is not sufficiently pure. The salt for analysis is obtained by saturating a solution of pure carbonate of sodium with hydrochloric acid, and crystallising.

a. *Chlorine.*—The powdered salt is strongly heated before weighing, to expel adhering moisture: it is then dissolved in water, the solution acidulated with nitric acid, and precipitated by nitrate of silver. By gentle warming and brisk agitation the chloride of silver soon subsides: it may be washed by decantation, or better on a filter, first with water acidulated with nitric acid, and finally with hot water, till the washings leave no residue on evaporation. It is then dried and ignited, with the filter-ash, in a weighed porcelain crucible, till it is in a state of tranquil fusion. When cool it is heated gently first with a drop or two of nitric, then of hydrochloric, acid, in order to re-convert into chloride any silver that may have been reduced by the filter: the excess of acid having been expelled by gentle heat, it is again fused, and weighed when cool. It may be weighed in an open crucible. ($ClAg : Cl :: 143{\cdot}5 : 35{\cdot}5$.)

b. *Sodium.* — Another weighed portion is gently heated in a weighed platinum crucible with concentrated sulphuric acid, till all the hydrochloric acid is expelled: it is then heated more strongly, to expel excess of sulphuric acid, and finally ignited, a fragment of carbonate of ammonium being placed in the crucible, to decompose any acid salt that may be formed. The resulting normal sulphate of sodium is weighed when cool. ($SO^4Na^2 : Na^2 :: 71 : 23$.)

Calculated percentage.

Cl 60·68 Na 39·32.

4. **Calc-Spar.** Carbonate of Calcium. CO^3Ca^2.

a. *Calcium.*—A weighed portion is dissolved in hydrochloric acid, care being taken that no loss is caused by effervescence: the solution is then saturated with ammonia, filtered if necessary, and the calcium precipitated as oxalate by oxalate of ammonium or potassium. The precipitate is allowed to stand for some hours in a warm place before filtration: it is then washed with hot water, dried, and gently ignited together with the filter-ash. If too strong a heat has been applied, the resulting carbonate of calcium may have been partially decomposed: if this is the case (which is known by its having an alkaline reaction) it is moistened with carbonate of ammonium, dried, again gently ignited, and weighed when cool. ($CO^3Ca^2 : Ca^2 : : 5 : 2$). Another method is to add sulphuric acid to the not too dilute hydrochloric solution of the compound, and then several times its volume of alcohol. The precipitated sulphate of calcium is washed with alcohol, dried, ignited, and weighed. ($SO^4Ca^2 : Ca^2 : : 17 : 5$.)

b. *Carbon and Oxygen.*—Another weighed portion is decomposed in a weighed apparatus for estimating carbonic anhydride, by moderately concentrated hydrochloric or nitric acid: the apparatus is again weighed, after the carbonic anhydride in it has been replaced by air, and the loss of weight represents the carbonic anhydride evolved; whence the amount of carbon and oxygen in the salt is given by the following proportion. ($Co^2 : CO^3 : : 11 : 15$.) (*See* p. 233.)

5. **Sulphate of Magnesium.** $SO^4Mg^2+7H^2O$.

a. *Magnesium.*—A weighed portion is dissolved in water, chloride of ammonium and ammonia added, and the magnesium precipitated by phosphate of sodium as phosphate of magnesium and ammonium. After standing for several hours in a warm place, the precipitate is filtered off, washed with a mixture of 3 pts. water and 1 pt. ammonia, dried, ignited with the filter-ash, and weighed. ($P^2O^7Mg^4 : Mg^4 : : 37 : 8$.)

b. *Sulphur and Oxygen.*—Estimated as in 1.

The salt does not lose all its water below about 230°.

Calculated percentage.

Hydrated salt,	SO^4 39·02	Mg^2 9·76	$7H^2O$ 51·22.
Dry ,,	SO^4 80·0	Mg^2 20·0.	

6. **Phosphate of Sodium.** $PO^4Na^2H+12H^2O$.

a. *Phosphorus and Oxygen.*—A weighed portion is dissolved in water, and the solution precipitated by a mixture of sulphate of magnesium, chloride of ammonium, and ammonia: the precipitate is treated as directed in 5. a. ($P^2O^7Mg^4 : PO^4 : : 222 : 95$.)

b. *Sodium.*—Acetate of ammonium is added to the aqueous solution of the salt, and then sesquichloride of iron till the appearance of a red tinge, and the whole heated to boiling: the precipitate is filtered off, and thoroughly washed with hot water.

(Or excess of sesquichloride of iron may be added at once, and, after filtration, the excess of iron in the filtrate removed by ammonia.) The filtrate is evaporated to dryness, the residue gently ignited, and either weighed as chloride, or converted into sulphate as in 3. b. (NaCl : Na : : 58·5 : 23.)

If the phosphoric acid be precipitated by a known volume of a standard solution of ferric chloride (containing a known amount of iron), the increase of weight of the ignited precipitate will give the amount of phosphorus and oxygen : the former determination may thus be controlled.

c. The *hydrogen* is determined by difference.

The salt does not lose all its water below about 300°.

Calculated percentage.

Hydrated salt,	PO^4 26·54	Na^2 12·85	H 0·28	$12H^2O$ 60·33.
Dry ,,	PO^4 66·9	Na^2 32·4	H 0·7	

7. **Acetate of Lead.** ($2(C^2H^3O^2Pb)+3H^2O=2$ atoms.)

a. *Lead.*—The aqueous solution of the salt is precipitated by carbonate of ammonium, with addition of a little free ammonia: the precipitated carbonate of lead is dried, converted into oxide of lead by ignition in a porcelain crucible, and weighed with the filter-ash. (Pb^2O : Pb^2 : : 223 : 207.) Or the solution is precipitated with moderately dilute sulphuric acid, which must be added in moderate excess ; the sulphate of lead is washed with water acidulated with sulphuric acid, and finally with alcohol, dried, ignited, and weighed. (SO^4Pb^2 : Pb^2 : : 303 : 207.) As oxide of lead is very easily reduced by carbonaceous matter, great care must always be taken in igniting lead-salts, to remove the precipitate from the filter as completely as possible before incinerating the latter : and the incineration must be complete before the filter-ash is added to the precipitate. It is perhaps safer not to ignite the precipitate at all, but to collect it on a filter which has been previously dried at 120° and weighed, to weigh the dried precipitate and filter together, and deduct the weight of the filter. Or the solid salt may be converted into sulphate of lead by evaporation with sulphuric acid with addition of a few drops of nitric acid, ignited, and weighed.

the process for organic analysis, by combustion with oxide of copper.

Calculated percentage.

C^4 12·66 H^6 1·58 O^4 16·89 Pb^2 54·62 $3H^2O$ 14·25.

8. **Tartrate of Potassium and Sodium.** (Rochelle Salt.) $C^4H^4O^6KNa+4H^2O$.

a. *Water.*—The estimation of the water requires the careful application of heat for some time. The salt fuses below 100°; boils at 120°; but does not lose all its water till heated to 215° (Wöhler.)

b. *Potassium and Sodium.*—The salt is ignited, the carbonaceous mass treated with dilute hydrochloric acid (or a solution of chloride of ammonium), and the carbon removed by filtration. The solution is evaporated to dryness, the residue (of mixed chlorides of potassium and sodium) gently ignited in a covered platinum crucible, and its weight determined. It is then dissolved in a little water, excess of bichloride of platinum added, and the whole evaporated to dryness in a water-bath; the residue is digested with alcohol, which leaves the chloroplatinate of potassium alone undissolved. This is collected on a weighed filter, washed with alcohol, dried at 100°, and weighed. ($PtCl^3K : K :: 244·5 : 39$.)

The sodium may be determined by deducting the weight of chloride of potassium from that of the mixed chlorides: but it is safer to control this result by a direct estimation. This is done by evaporating the alcoholic filtrate (which should have a distinct yellow colour) to dryness, decomposing the residue of chloroplatinate of sodium, by ignition in a covered crucible with a few crystals of pure oxalic acid, dissolving out the chloride of sodium with water, filtering off the metallic platinum, evaporating the filtrate to dryness, and weighing the residue after gentle ignition. (6. b.)

c. *Carbon, Hydrogen, and Oxygen.*—Determined by combustion with oxide of copper, with addition of some phosphate of copper.

Calculated percentage.

Hydrated salt,	C^4 17·02	H^4 1·42	O^6 34·04	K 13·83	Na 8·16	$7H^2O$ 25·53.
Dry ,,	C^4 22·86	H^4 1·9	O^6 45·72	K 18·57	Na 10·95.	

9. Sulphates of Barium, Strontium, and Calcium.

Heavyspar, SO^4Ba^2. Celestine, SO^4Sr^2. Gypsum, $SO^4Ca^2 + 2H^2O$.

a. *Water.*—The water in gypsum is determined by ignition.

b. *Sulphur and Oxygen.*—Sulphate of calcium is completely converted into carbonate by boiling with a solution of carbonate of sodium: the solution contains all the sulphuric acid. The sulphates of barium and strontium are not completely decomposed in this manner: they must be finely powdered, and fused in a platinum crucible with four times their weight of the mixed carbonates of potassium and sodium, the fused mass treated with boiling water, the earthy carbonates filtered off, the filtrate acidulated with hydrochloric acid, and precipitated by chloride of barium, as in 1. c.

c. If only *barium* be present, the carbonate, thoroughly washed, is dissolved in dilute hydrochloric acid, and precipitated hot by dilute sulphuric acid. If *strontium* be present also, the barium is precipitated first from the hydrochloric acid solution by fluosilicic acid, with addition of alcohol, and the fluosilicate of barium collected on a weighed filter, dried at 100°, and weighed. ($SiF^6Ba^2 : Ba^2 :: 279{\cdot}7 : 137{\cdot}2$.) The filtrate is evaporated to dryness with excess of sulphuric acid, and the residue of sulphate of strontium ignited and weighed. ($SO^4Sr^2 : Sr^2 :: 91{\cdot}9 : 43{\cdot}9$.) Barium may also be separated from strontium, in a dilute neutral solution, by bichromate of potassium, which precipitates the barium only. If *calcium* and *barium* be present, the solution is largely diluted, and the barium precipitated by sulphuric acid: the filtrate is then neutralised by ammonia, and the calcium precipitated by oxalate of ammonium (4. a). If *barium*, *strontium*, and *calcium*, be present, the carbonates are dissolved in nitric acid, care being taken to obtain a solution as nearly neutral as possible, which is then evaporated to dryness in a flask: the residue is digested for some time in the corked flask with absolute alcohol in the cold, by which the nitrate of calcium is alone dissolved. The filtrate is diluted with water, most of the alcohol evaporated off, and the calcium precipitated as oxalate: the nitrates of barium and strontium are dissolved in water, and the metals separated as above.

The sulphates of strontium and calcium are entirely converted into carbonates by digestion in the cold with a frequently renewed solution of carbonate of ammonium or potassium; while sulphate of barium is not so decomposed. This reaction is employed for both qualitative and quantitative separation of the three metals. The mixed carbonates and sulphate are treated with dilute hydrochloric acid, which dissolves the strontium and calcium as chlorides, and leaves the sulphate of barium undissolved.

Calculated percentage.

Sulphate of barium - -	SO^4 41·17	Ba^2 58·83.	
„ strontium - -	SO^4 52·23	Sr^2 47·77.	
„ calcium, hydrated	SO^4 55·81	Ca^2 23·26	$2H^2O$ 20·93.
„ „ dry -	SO^4 70·59	Ca^2 29·41.	

10. **Dolomite, Bitter-spar.** (Carbonate of calcium and magnesium, frequently carbonate of iron also.)

The mineral, dried at 100°, is dissolved in hydrochloric acid (in a flask or covered beaker), a little nitric acid added, and the whole heated, in order to convert the iron into sesquisalt: chloride of ammonium and a slight excess of ammonia are then added, and any ferric oxide that may be precipitated filtered off rapidly. The calcium is then precipitated from the filtrate as oxalate (4. a), and the magnesium as double phosphate (5. a). If the mineral contains any silica, it is left undissolved by the hydrochloric acid, and is separated by filtration. The ferric oxide precipitated by ammonia, generally contains some magnesium and (if the ammonia contain any carbonate) some calcium: in very accurate analyses, the iron should be precipitated as in 11. The carbon and oxygen are estimated by difference: or directly, with a fresh portion of mineral, as in 4. b.

11. **Spathic Iron-ore.** (Carbonate of iron, frequently containing carbonates of manganese, calcium, and magnesium.)

The mineral, finely powdered and dried, is dissolved in hot hydrochloric acid, nitric acid or chlorate of potassium being added from time to time, so as to convert all the iron into sesquisalt. The solution is then nearly neutralised with carbonate of sodium, a saturated solution of acetate of sodium added, and the whole heated, when all the iron is precipitated; it is filtered from the *hot* solution, washed with hot water, dried, ignited, and weighed as sesquioxide (2. a). The filtrate is mixed with a slight excess of hypochlorite of sodium, acidulated with acetic acid, and allowed to stand for 24 hours, when all the manganese is precipitated as binoxide. If the supernatant liquid has a red tinge, owing to the formation of some permanganic acid, a few drops of alcohol must be added, and it must not be filtered till it is colourless. The precipitate is converted into manganoso-manganic oxide, Mn^6O^4, by ignition, and weighed. ($Mn^6O^4 : Mn^6 :: 55 : 39$.) In the filtrate calcium and magnesium are determined, as in 10.

Another method, especially applicable where but little manganese is present, is to dissolve the mineral as before, to add ammonia to the solution until a permanent precipitate is just formed, and to precipitate the iron by neutral succinate of ammonium: the precipitate is filtered off rapidly, washed with cold water, dried, ignited in a porcelain crucible, and weighed as ferric oxide. The filtrate is acidulated with hydrochloric acid, evaporated to dryness, and heated till the ammoniacal salts are expelled: the residue is dissolved in dilute hydrochloric acid, the solution saturated with chlorine, the manganese precipitated as sesquihydrate by ammonia, filtered off as rapidly as possible to avoid the formation of carbonate of calcium, and converted into Mn^6O^4 by ignition, as before. The calcium and magnesium are then determined in the filtrate.

12. **Copper-pyrites.** (Sulphide of copper and iron.)

The powdered mineral is heated (not to boiling) with aqua-regia in a small flask, until the sulphur which separates out is of a pure yellow colour: the flask should be placed obliquely over the lamp, so as to avoid loss from possible ebullition. If the sulphur is fused into globules, it may be separated by decantation; if it is in the form of a powder, it must be collected on a weighed filter it is thoroughly washed, dried in a porcelain crucible at a very gentle heat, and weighed. It should then be burnt, to see if it contains any metal, or quartz, &c., the weight of which, if found, must be deducted. The sulphur that has been oxidised into sulphuric acid is then precipitated from the solution by chloride of barium, as in 1. c, and its weight added to that of the undissolved sulphur. ($SO^4Ba^2 : S :: 233{\cdot}2 : 32$.) The filtrate is freed from excess of barium by dilute sulphuric acid, and the copper completely precipitated by hydrosulphuric acid. The sulphide of copper is filtered off as rapidly as possible, washed with water containing hydrosulphuric acid, dried on the filter, detached as far as possible and thrown into a beaker, the filter being incinerated separately, and its ash added to the precipitate. The whole is then heated with strong nitric acid until the separated sulphur is of a pure yellow colour: the solution is diluted and filtered, and the copper precipitated from the filtrate by potash, as in 1. b. The filtrate from the sulphide of copper is heated, nitric acid being added from time to time to convert all the iron into sesquisalt, which is then precipitated by ammonia, as in 2. a.

13. **Zinc-blende.** (Sulphide of zinc, generally contains iron, sometimes copper and cadmium.)

The mineral is dissolved, and the sulphur estimated, as in 12. The solution, freed from barium by dilute sulphuric acid, is saturated with hydrosulphuric acid, which precipitates the copper and cadmium as sulphides; these are filtered off, dissolved together with the filter in nitric acid, the solution saturated with potash, and hydrocyanic acid added till the precipitate formed is redissolved. From this solution the cadmium is precipitated by hydrosulphuric acid: the filtrate, containing the copper, is boiled with aqua-regia, and precipitated by potash (1. b). The sulphide of cadmium is dissolved in nitric acid, and the cadmium precipitated as carbonate by carbonate of sodium, dried, converted into oxide by ignition, and weighed. ($Cd^2O : Cd^2 :: 8 : 7$.) The filtrate from the sulphides is boiled, hypochlorite of sodium being added to convert all the iron into sesquisalt, neutralised with ammonia, and the iron precipitated by succinate of ammonium

(11). If the iron be precipitated at once by ammonia, it carries down some zinc. From the filtrate, the zinc is precipitated by sulphide of ammonium[*]: the sulphide of zinc is washed with water containing a little sulphide of ammonium, dissolved while moist (with the filter) in hot hydrochloric acid, and the hot solution precipitated by carbonate of ammonium. The carbonate of zinc, when ignited, is converted into zinc-oxide, and so weighed. ($Zn^2O : Zn^2 :: 81 : 65$.)

14. **Alloy of Copper and Zinc.** (Brass.)

The metal is dissolved in hydrochloric acid, with gradual addition of nitric acid, the solution diluted, and precipitated by hydrosulphuric acid: the sulphide of copper is treated as in 12. The filtrate is heated to boiling, to expel free hydrosulphuric acid, and the zinc precipitated from the hot solution by carbonate of sodium (13). Or the dilute solution of the alloy is neutralised with ammonia, and digested with a slight excess of solid potash till the colour and ammoniacal smell have disappeared: the precipitated cupric oxide is filtered off, and the zinc precipitated from the filtrate by sulphide of ammonium (13). If the brass contains tin, it should be dissolved in nitric acid, when the tin remains undissolved as binoxide. Brass frequently contains traces of lead, which would be precipitated with the copper by hydrosulphuric acid, and may be detected by evaporating to dryness the solution of sulphide of copper in nitric acid, and treating the residue with water, when the sulphate of lead remains undissolved.

15. **Alloy of Copper and Tin.** (Bronze, Bell-metal, Gun-metal.)

The alloy is finely divided and oxidised with concentrated nitric acid, most of the free acid evaporated off, hot water added, and the undissolved binoxide of tin filtered off, washed, dried, ignited, and weighed. ($SnO^2 : Sn :: 150 : 118$.) The copper is precipitated from the filtrate by potash (1). If the alloy contain lead, iron, and zinc, the lead is precipitated (after filtering off the stannic oxide) by sulphuric acid, then the copper by hydrosulphuric acid, and the zinc and iron separated as in 13. The binoxide of tin separated by the above method is not quite free from copper. A more accurate method is to dissolve the alloy in weak aqua-regia, to precipitate with carbonate of sodium, to heat the whole to boiling, to acidulate with nitric acid, and allow the whole to digest for some time; when the binoxide of tin remains undissolved.

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[*] If no ammoniacal salts be present, the zinc may be precipitated at once by

Another method is to heat the alloy in a bulb-tube in a stream of dry chlorine, when the tin (and part of the iron) are volatilised as chlorides: they are received in dilute hydrochloric acid, and the tin precipitated as sulphide, which is converted into oxide by ignition. The residual chlorides of copper and lead are reduced by hydrogen, the metals dissolved in nitric acid, and separated as in 14.

16. **Alloy of Copper, Zinc, and Nickel.** (German Silver.)

The alloy is dissolved in nitric acid, most of the free acid evaporated off, and the copper precipitated from the dilute solution by hydrosulphuric acid (12). The filtrate is boiled, and the nickel and zinc precipitated hot by carbonate of sodium. The precipitate is ignited, powdered, and heated in a stream of dry hydrogen as long as any water is formed, whereby the nickel alone is reduced: the mixture of metallic nickel and oxide of zinc is digested for 24 hours with a concentrated solution of carbonate of ammonium, which dissolves the oxide of zinc: the metallic nickel is washed, dried, and weighed. The zinc solution is evaporated to dryness, ignited, and weighed as oxide. Or, the filtrate from the sulphide of copper is concentrated by evaporation, mixed with excess of potash, and hydrocyanic acid added till the precipitate is dissolved: from this solution sulphide of potassium (not sulphide of ammonium) precipitates the zinc alone as sulphide: the precipitate is treated as in 13. The filtrate is boiled with aqua-regia, and precipitated while hot with potash: the precipitate is washed with hot water, dried, ignited, and weighed as oxide of nickel. ($Ni^2O : Ni^2 :: 37 : 29$.)

17. **Alloy of Silver and Copper.** (Silver Coins.)

The alloy is dissolved in nitric acid, and the silver precipitated from the solution by hydrochloric acid: the chloride of silver is treated as in 3. a. ($AgCl : Ag :: 143{\cdot}5 : 108$.) The copper is precipitated from the filtrate by potash (1. b). If the alloy contain any gold, it remains undissolved by the nitric acid as a brown powder.

18. **Alloy of Gold with Silver or Copper.** (Gold coins, &c.)

a. *Gold and Silver.*—The methods of analysing these alloys vary according to the proportion of each metal present. An alloy containing less than 15 per cent. silver may be treated with aqua-regia, which dissolves all the gold, leaving the silver as chloride: the gold is precipitated from the solution, in the metallic state, by oxalic acid or ferrous sulphate, washed, ignited, and weighed as metal. An alloy containing more than 80 per cent. silver may be treated with nitric acid, which dissolves all the silver, leaving metallic gold: the silver is precipitated as chloride: the gold should be dissolved in aqua-regia, to ascertain whether it contains any trace of silver, and precipitated as above. The alloy must be finely laminated in both these cases. Alloys containing between 15 and 80 per cent. silver must be fused in a porcelain crucible with 3 times their weight of pure lead: from the alloy thus formed nitric acid dissolves all the silver and lead, leaving the gold. The silver is precipitated by hydrocyanic acid, or from the very dilute boiling solution by hydrochloric acid. Cyanide of silver must be collected on a weighed filter, dried at 100°, and weighed ($AgCN : Ag :: 67 : 54$).

All alloys of gold and silver, whatever the relative proportions of the two metals, may be analysed by heating the thinly laminated alloy with concentrated sulphuric acid until all evolution of gas has ceased; the sulphate of silver is then dissolved out with hot water, and the residue of metallic gold washed, ignited, and weighed.

b. *Gold and Copper.*—The alloy is dissolved in aqua-regia and the gold precipitated from the solution (which must not contain any free nitric acid) by oxalic acid: the copper is then precipitated from the filtrate by potash (1. b). Or the gold may be precipitated by ferrous sulphate, and then the copper by hydrosulphuric acid.

19. **Alloy of Tin and Lead** (Pewter, soft solder); **of Tin, Lead, and Bismuth.** (Fusible metal.)

a. *Tin and Lead.*—The alloy is powdered, and oxidised with moderately strong nitric acid, which converts the tin into insoluble binoxide; water is added, and the stannic oxide filtered off, dried, ignited, and weighed (15). The filtrate is evaporated, with addition of dilute sulphuric acid, till all the nitric acid is expelled: the sulphate of lead is filtered off, and treated as in 7. a.

b. *Tin, Lead, and Bismuth.*—The alloy is treated as above: the stannic oxide must be washed with water acidulated with nitric acid to dissolve any basic bismuth-salt that has been precipitated by dilution. The filtrate is treated as above with sulphuric acid, and the sulphate of lead washed with water containing sulphuric acid; the bismuth is then precipitated by carbonate of ammonium, the whole allowed to stand for some time till the precipitate is completely separated, when it is filtered off, washed, dried, ignited, and weighed as bismuthic oxide. ($Bi^2O^3 : Bi^2 :: 29 : 26$.)

20. **Alloy of Antimony and Lead.** (Type-metal.)

The finely-divided alloy is oxidised with moderately strong nitric acid, ammonia added in slight excess, and then excess of yellow sulphide of ammonium, with which the whole is digested out of contact with the air, until the precipitate is perfectly black. This precipitate, which contains all the lead as sulphide, is collected on a weighed filter, washed with weak sulphide of ammonium, and finally with water, dried carefully at a gentle heat, and weighed ($Pb^2S : Pb^2 :: 239 : 207$); or, as the sulphide of lead may contain free sulphur, it is safer to convert it into sulphate by treatment with strong nitric acid. From the filtrate, the sulphide of antimony is precipitated by dilute sulphuric acid, collected on a weighed filter, dried, and weighed. In order to estimate the antimony, a weighed portion of the sulphide is oxidised by concentrated nitric acid, and hydrochloric acid added till all the antimony is dissolved: enough tartaric acid is then added to prevent precipitation by dilution, and the whole diluted with water; and the amount of sulphur determined, as in 12, by weighing the unoxidised sulphur, and precipitating the oxidised sulphur by chloride of barium. From this the amount of sulphur, and consequently that of antimony, is calculated for the total weight of the precipitated sulphide of antimony. A simpler method is that recommended by Bunsen (p. 94), of oxidising the sulphide of antimony by fusion with mercuric oxide, and estimating the antimony as Sb^4O^8. ($Sb^4O^8 : Sb^4 :: 19 : 15$.)

Arsenic and lead are separated in a similar manner: the sulphide of arsenic, however, is converted into arsenic acid by solution in hydrochloric acid with addition of chlorate of potassium, and precipitated by sulphate of magnesium (after addition of ammonia and chloride of ammonium) as arsenate of magnesium and ammonium; which, after standing 24 hours, is collected on a weighed filter, washed with dilute ammonia, dried at 100°, and weighed. ($AsO^4Mg^2(NH^4)+\frac{1}{2}H^2O : As :: 38 : 15$.)

21. **Cobalt-glance.** (Sulphide and arsenide of cobalt: generally containing nickel and iron, sometimes manganese and quartz.) *Speiss-cobalt* (arsenide of cobalt, with small quantities of nickel, iron, and copper). *Copper-nickel* (arsenide of nickel; also cobalt and iron). The smelting-products, called *cobalt-* and *nickel-speiss*, contain the same elements, and frequently copper and bismuth.

The same methods of analysis apply to all these minerals.

a. The mineral is very finely powdered and carefully mixed with 6 times its weight of a mixture of 2½ parts nitre, and 3 parts carbonate of sodium, in a porcelain crucible: it is then fused for some time at a dull red heat, the fused mass digested with water, and the metallic oxides filtered off and thoroughly washed.* The filtrate, which contains all the arsenic as arsenate, and all the sulphur as sulphate, of sodium, besides some alkaline carbonate, is acidulated with hydrochloric acid, chloride of barium added, and the sulphur calculated from the weight of the sulphate of barium precipitated (12). The filtrate is freed from excess of barium by dilute sulphuric acid, chloride of ammonium and ammonia added, and then sulphate of magnesium, which precipitates the arsenic as arsenate of magnesium and ammonium (20). The metallic oxides are dissolved in concentrated hydrochloric acid, the ashes of the filter being added to the solution, and the copper and bismuth precipitated by hydrosulphuric acid: the sulphides are washed with water containing hydrosulphuric acid, dissolved in nitric acid, and the two metals separated by carbonate of ammonium, which precipitates only the bismuth (19). The filtrate from the sulphides is heated, chlorate of potassium being added, to convert the iron into sesquisalt, and the iron precipitated by succinate of ammonium (11). From the filtrate the cobalt and nickel are precipitated by potash at a boiling heat, and separated as at p. 148. If the two oxides be reduced by hydrogen, and the reduced metal weighed before dissolving it in hydrochloric acid, the direct determination of the cobalt will not be necessary. If manganese be present, the oxides precipitated by potash are converted into sulphides by heating them in a small porcelain boat in a stream of hydrosulphuric acid: the sulphides when cold are treated with very dilute hydrochloric acid, which dissolves the sulphide of manganese, leaving those of nickel and cobalt undissolved. The separation is not quite so exact when the sulphides precipitated by sulphide of ammonium are treated with acetic acid. The manganese is precipitated by carbonate of sodium, ignited, and weighed as Mn^6O^4 (11). If the mineral contain any quartz, it is left behind when the oxides are dissolved in hydrochloric acid.

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* If the contents of the crucible are allowed to cool completely before adding water, the crucible invariably breaks. This is prevented by carefully introducing the crucible, while its contents are still at a temperature of 100°—120°, edgeways into a porcelain basin of hot water, when the contents are readily dissolved out without injury to the crucible.

b. The finely-powdered mineral may be oxidised by gradually heating it with 3 parts chlorate of potassium and 3 parts carbonate of sodium, until the whole is in a state of tranquil fusion: this may be done in a platinum crucible, the bottom of which has been covered with carbonate of sodium. The fused mass is treated as in (a).

c. The mineral may be dissolved in concentrated hydrochloric acid with gradual addition of nitric acid, the undissolved sulphur filtered off, and the sulphuric acid formed precipitated by chloride of barium (12). The filtrate, freed from excess of barium, is heated with sulphurous acid till it no longer smells of sulphurous anhydride, and saturated at a gentle heat with hydrosulphuric acid. The sulphide of arsenic is filtered off after 24 hours, dissolved in aqua-regia, and the arsenic precipitated as in (a). The filtrate is treated as in (a).

d. If the mineral contain lead and silver, it may be advantageously analysed by means of chlorine, as in the case of fahl-ore (22).

22. **Fahl-ore.** (Sulphides of antimony, arsenic, copper, silver, mercury, iron, and zinc.)

All these metals are not found in every specimen of fahl-ore: different specimens vary considerably both in the number and relative proportion of their constituents.

The finely-powdered mineral is introduced into a double bulb-tube, one end of which is bent at a right angle, care being taken that all the mineral is contained in the bulb which is farthest from the bent end. The straight end of the tube is then connected with an apparatus for the evolution of perfectly dry chlorine; and the bent end is introduced air-tight into a receiver — a large U tube answers the purpose — containing a mixture of dilute hydrochloric and tartaric acids: a bent tube is connected with the other end of the U tube, by which the excess of chlorine is conducted into methylated spirit. The bulb-tube should not be attached to the chlorine apparatus till all the atmospheric air has been driven out of the latter. A very slow stream of chlorine is then passed through the tube, which decomposes the fahl-ore with considerable evolution of heat: and when the bulb containing the mineral has cooled, it is heated gently in order to separate the volatile chlorides, which must be driven beyond the space between the two bulbs. Those elements which are volatilised as chlorides are *sulphur*, *arsenic*, *antimony*, *mercury*, part of the *iron* (and, if too strong a heat has been applied, some of the *zinc*): those which remain in the bulb as non-volatile chlorides are *copper*, *silver*, *zinc*, and most of the *iron*.

For the analysis of the *volatile* chlorides, the bulb-tube is divided between the two bulbs, and the portion containing the sublimate covered with a wide tube, closed at one end, and moistened on the inside with water, in which position it is left for 24 hours. The sublimate thus absorbs water gradually, and may then be dissolved out with water, without the evolution of heat and probable loss which would ensue if this precaution were neglected. The tube being thoroughly rinsed out, the solution is added to the liquid in the receiver: any sulphur that separates is filtered off, and any antimony that precipitates is dissolved by heat. The acid solution is then saturated with hydrosulphuric acid, the washed precipitate digested with sulphide of ammonium, the undissolved sulphide of mercury collected on a weighed filter, dried at 100°, and weighed. ($Hg^2S : Hg^2 :: 29 : 25$.) The sulphides of antimony and arsenic are precipitated from the sulphide of ammonium solution by dilute sulphuric acid, and the metals separated as at p. 93. The filtrate (containing tartaric acid) is neutralised by ammonia, sulphide of ammonium added, the precipitated sulphide of iron filtered off, washed with water containing hydrosulphuric acid, dissolved in hydrochloric acid, the solution heated with nitric acid, and the iron precipitated by ammonia (2. a).

The bulb containing the *non-volatile* chlorides is digested with dilute hydrochloric acid till only chloride of silver remains undissolved: this is weighed as in 3. a. From the solution the copper is precipitated by hydrosulphuric acid (12): the iron and zinc in the filtrate are separated as in 13.

The sulphur is best estimated in a separate portion of the ore, which is oxidised by careful fusion with 3 parts chlorate of potassium and 3 parts carbonate of sodium (21. b): the fused mass is digested with water, the solution acidulated with hydrochloric acid, and precipitated by chloride of barium (1. e).

This mode of analysis is applicable to bournonite (sulphides of antimony, lead, and copper); red silver-ore (sulphides of antimony or arsenic and silver); and other minerals resembling fahl-ore in composition. If lead be present, the chlorides must be volatilised at a very gentle heat, when the lead will remain with the non-volatile chlorides: and when these chlorides are treated with dilute hydrochloric acid, a large quantity of water must be added, to ensure the solution of the chloride of lead.

23. **Mesotype** or **Natrolite**. (Silicate of aluminium and sodium, containing water of crystallisation.)

The water is determined by igniting a weighed portion of the finely divided mineral, which has been dried at 100°.

Another portion, dried at 100° but not ignited, is digested with concentrated hydrochloric acid in a porcelain basin, until all that is undissolved is converted into a jelly, in which no gritty particles can be detected by rubbing with a glass rod. It is then evaporated to complete dryness on a waterbath, with frequent stirring, the residue moistened with hydrochloric acid and allowed to stand for half an hour without heating, and then digested with hot water. The silica is filtered off, washed till the washings give no cloudiness with nitrate of silver, *completely* dried, ignited (with the filter), and weighed. ($SiO^2 : Si :: 60{\cdot}5 : 28{\cdot}5$.) From the filtrate the aluminium is precipitated as hydrate by sulphide (or carbonate) of ammonium, washed with hot water, dried, strongly ignited, and weighed. ($Al^4O^3 : Al^4 :: 102{\cdot}4 : 54{\cdot}4$). The filtrate from the alumina is evaporated to a small bulk, transferred to a weighed platinum crucible, carefully evaporated to dryness, and heated till ammoniacal salts are expelled; the residual chloride of sodium is ignited gently, and weighed (6. b). If the mineral contain any iron, it will be precipitated as sulphide by the sulphide of ammonium, and will give a more or less black tinge to the alumina. In order to estimate it the precipitate is dissolved in hydrochloric acid, heated to boiling, sulphite of sodium added, and then excess of caustic soda, and the whole boiled till the precipitate is black and pulverulent. This black precipitate (ferrosoferric oxide) is filtered off, dissolved in hydrochloric acid, nitric acid added and the whole boiled, and the iron precipitated by ammonia (2. a). From the acidulated filtrate the aluminium is precipitated as above. The alumina and ferric oxide, after weighing, should be treated again with hydrochloric acid, as they frequently contain small quantities of silica, the weight of which must be deducted, and added to that of the silica previously obtained. Similarly, the purity of the silica obtained in the analysis of a silicate should always be tested by carbonate of sodium or hydrofluoric acid: pure silica dissolves entirely in the former, and when dissolved in the latter leaves no residue on evaporation.

In silicate analyses, calculate the *silicon* and *metals* separately: the *oxygen* is determined by difference.

24. **Prehnite.** (Silicate of calcium and aluminium, containing water of crystallisation.)

The same portion in which the water has been determined by ignition is decomposed by hydrochloric acid, and the silica and aluminium separated as in 23. Air should be excluded as far as possible during the filtration of the alumina, which must be precipitated by sulphide of ammonium: from the filtrate the calcium is precipitated as oxalate (4. a). As the alumina thus separated generally contains both silica and lime, it must, after weighing, be redissolved in hydrochloric acid, evaporated to dryness, and the above process of separation repeated: the weights of silica and calcium obtained being deducted from that of the alumina and added to the former amounts. If iron be present it is separated as in 23. Stilbite (a mineral containing the same elements as prehnite) is analysed in the same manner, excepting that (as in mesotype and most other zeolites) the portion decomposed by hydrochloric acid must not have been ignited.

25. **Olivine.** (Silicate of iron and magnesium: contains also traces of nickel and manganese, frequently of copper and tin.)

The mineral is decomposed and the silica separated as in 23. The filtrate is saturated with hydrosulphuric acid, which precipitates copper and tin as sulphides: the filtrate from which is concentrated by evaporation, boiled with chlorate of potassium, and the iron precipitated by succinate of ammonium or carbonate of barium (11). The nickel and manganese are then precipitated by sulphide of ammonium, excess of which must be avoided: the precipitate is allowed to subside completely, filtered off, washed with very dilute sulphide of ammonium, and treated on the filter with very dilute hydrochloric acid, which dissolves only the sulphide of manganese. The sulphide of nickel is ignited in the air and weighed as oxide (16): the manganese is precipitated by carbonate of sodium at a boiling heat, ignited, and weighed as Mn^6O^4 (11). Finally the magnesium is precipitated by phosphate of sodium (5. a).

26. **Felspar.** (Silicate of aluminium and potassium).

a. *Silicon and Aluminium.*—The mineral is very finely powdered, dried at about 200°, and intimately mixed in a platinum crucible with 4 times its weight of a mixture of carbonates of potassium and sodium, and fused for half an hour at a strong red heat. When cool the crucible is placed in a beaker, digested with very dilute hydrochloric acid, the beaker being covered with a glass plate to prevent loss by spurting. When the fused mass is completely removed from the crucible, the contents of the beaker are transferred to a porcelain basin, evaporated to dryness with excess of hydrochloric acid, and the silicon, aluminium (and iron, if present), determined as in 23. If the felspar contain calcium (as labradorite, anorthite), the aluminium is precipitated by sulphide of ammonium, and the calcium from the filtrate by oxalate of ammonium (4. a).

b. *Potassium.*—A second portion of the powdered mineral is decomposed by hydrofluoric acid in a platinum dish, either by digesting it with the liquid acid, or by exposing it, moistened with dilute sulphuric acid, to the vapours of the acid evolved from fluorspar and sulphuric acid in an appropriate leaden vessel (p. 54). When the decomposition is complete, concentrated sulphuric acid is cautiously added, the whole evaporated to dryness, and heated till all the fluorine and silicon are volatilised, and the excess of sulphuric acid expelled. The residue is moistened with concentrated sulphuric acid, and water added, in which it should dissolve completely, and the aluminium and iron separated as above. The filtrate is evaporated to dryness, heated to expel the ammoniacal salt, a fragment of carbonate of ammonium being placed in the hot crucible to prevent the formation of an acid sulphate; and the residual normal sulphate of potassium weighed. ($SO^4K^2 : K^2 :: 87 : 39$.) If sodium be present also, the mixed sulphates are converted into chlorides by repeated ignition with chloride of ammonium until their weight is constant, and the metals separated as in 8.

Another method, which, like the preceding one, will serve either for the complete analysis of the felspar, or for the estimation of its alkaline metals only, is to treat the mineral as in (a), substituting carbonate of barium for the alkaline carbonates: or it may be fused in a silver crucible with hydrate of barium. After the separation of the silica, the barium is removed by dilute sulphuric acid (excess of which must be avoided), and the analysis proceeded with as above. It is essential to the success of this method that the mineral be reduced to a perfectly impalpable powder, that the mixture with the flux be as intimate as possible, and that the fusion be effected at an intense white heat. Whenever a sufficient quantity of the mineral is at hand, it is preferable to analyse it in two distinct portions, as directed above.

27. **Glass.** (Silicate of calcium and potassium or sodium, frequently also of lead; often contains iron, manganese, aluminium, and magnesium).

Glass is analysed in the same manner as felspar. One portion is taken for the determination of all the elements except the alkaline metals, and fused with alkaline carbonates. After the separation of the silica, the lead is removed by hydrosulphuric or sulphuric acid: chlorine-water is added to the filtrate and then ammonia, which precipitates iron, manganese, aluminium, and perhaps magnesium. The calcium is then precipitated by oxalate of ammonium (4. a), and the filtrate tested for magnesium by phosphate of sodium.

A second portion is decomposed by hydrofluoric acid, or by fusion with carbonate of barium, for the determination of the alkaline metals (26).

28. **Augite, Hornblende, Garnet, Idocrase, Epidot.*** (Silicates of iron, manganese, aluminium, calcium, and magnesium.)

The finely powdered mineral is fused with 4 parts alkaline carbonates, the fused mass treated with hydrochloric acid, with addition of a few drops of nitric acid, and the silica separated as in 26. The filtrate is treated with chlorine-water and ammonia, which precipitates iron, manganese, aluminium, and perhaps magnesium: after which the calcium is precipitated by oxalate of ammonium, and the magnesium by phosphate of sodium. The precipitate by ammonia is dissolved in hydrochloric acid, heated to boiling in order to convert all the manganese into protochloride, largely diluted, and gradually neutralised by carbonate of sodium, with constant stirring: the iron and aluminium are thus precipitated, filtered off, and separated as in 23. From the filtrate, which contains the manganese and magnesium as acid carbonates, the manganese is precipitated by hypochlorite of sodium, as in 11: and the magnesium, after concentration, by phosphate of sodium. Carbonate of barium may also be employed to precipitate the iron and aluminium.

29. **Bone-earth.** (Normal phosphates of calcium and magnesium, carbonate and fluoride of calcium.)

In order to estimate the amount of bone-earth, or ash, contained in bones, a portion of the bone is carefully cleaned, powdered, digested with water, and dried at 150°. A weighed portion of the powder is then ignited until it is perfectly white, when it consists of nothing but bone-earth. Another portion of the dry powder is taken for the determination of the carbonic acid by loss (4. b).

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* Garnet, idocrase, and epidot are completely decomposed by hydrochloric acid after ignition.

A portion of the perfectly white earth is dissolved in hydrochloric acid, heated for some time to expel all the carbonic acid, saturated with ammonia, the precipitate redissolved in as little hydrochloric acid as possible, and acetate of sodium added. Traces of iron are generally thus precipitated as phosphate, and must be filtered off and estimated: but if a more abundant white precipitate is formed, dilute hydrochloric acid is added till it is entirely redissolved. From the solution the calcium is then precipitated by oxalate of potassium (4. a): the filtrate is saturated with ammonia. which precipitates all the magnesium (together with the amount of phosphoric acid corresponding to it) as phosphate; this is filtered off, ignited, and weighed, and the rest of the phosphoric acid precipitated from the filtrate by sulphate of magnesium, chloride of ammonium, and ammonia (6. a).

Another method is to heat the bone-earth with moderately strong nitric acid, together with a weighed quantity of pure metallic tin, from two to three times the weight of the earth. All the phosphoric acid in the earth combines with the tin, forming an insoluble compound, which is filtered off after dilution, dried, ignited, and weighed. The excess of weight of this residue over that of the tin employed, represents the phosphorus and oxygen of the phosphoric acid. The calcium and magnesium are determined in the filtrate as usual. A more accurate method of estimating the phosphoric acid is by transferring the insoluble phosphate of tin, washed by decantation, to a platinum dish, dissolving it in the smallest possible quantity of caustic potash, saturating the solution with hydrosulphuric acid, adding sulphide of ammonium, and acidulating feebly with acetic acid. The whole is then transferred to a weighed flask of about 1 litre capacity, diluted with water, and the full flask weighed. After about twelve or sixteen hours' standing, the clear solution is passed through a filter, concentrated, and the phosphoric acid precipitated as phosphate of magnesium and ammonium. The flask is then weighed again, in order to determine the weight of the liquid poured off. It is then only necessary to ascertain the weight of the sulphide of tin, either directly or by calculation, in order to be able to calculate the total amount of phosphoric acid.

The fluorine is either determined in a separate portion by the process given at p. 47; or by calculation, by deducting from the total weight of calcium obtained the amount which was contained in the earth as carbonate and phosphate; the excess of calcium was contained as fluoride. ($\mathrm{CaF} : \mathrm{F} :: 39 : 19$.)

30. **Ashes,** animal or vegetable. (Salts of iron, magnesium, calcium, potassium, sodium (rarely manganese and aluminium); generally carbonates, silicates, sulphates, phosphates, chlorides (rarely bromides, iodides, and fluorides).

The vegetable or animal matter is incinerated until the carbonaceous matter is completely burnt, and the residue is quite white: the occasional addition of a drop of nitric acid facilitates the combustion of the carbon. If the substance were previously dried at 100° and weighed, the weight of the ash will give the percentage of inorganic constituents. The ash should be finely powdered and kept in a stoppered bottle.

a. *Carbonic acid* is determined by loss (4. b) in a portion of the ash which has been incinerated without the addition of nitric acid.

b. *Chlorine* (*Bromine*, *Iodine*).—A second portion of the ash is digested with water acidulated with nitric acid, and the chlorine precipitated from the filtrate by nitrate of silver (3. a).

c. *Silicon and other constituents.*—A larger portion of the ash is decomposed by excess of hydrochloric acid, and the silica separated as in 23. When, as is often the case, the ash contains carbon or sand, these will remain with the silica, which should therefore, after weighing, be digested with dilute potash in a platinum crucible till all the silica is dissolved, except that existing as sand. The residue is collected on a weighed filter, weighed, and its weight deducted from that of the silica, and from that of the ash employed. By evaporation to dryness with hydrochloric acid, the silica may be separated again from the alkaline solution. The filtrate containing all the other constituents of the ash is measured or weighed, and divided into three portions, whose volume or weight is ascertained. In one portion the sulphuric acid is estimated by chloride of barium (1. c): in another, the alkaline metals (8): in the third, the other metals and the phosphoric acid (28, 29).

When, as is the case with the ashes of seeds, the whole or the greater part of the ash consists of phosphates, the analysis proceeds as in 29: the filtrate from the silica is saturated with ammonia and then with acetic acid, when the iron and part of the phosphoric acid are precipitated as phosphate; then the calcium is precipitated by oxalate of potassium: then another part of the phosphoric acid and all the magnesium by ammonia: and then the rest of the phosphoric acid by a magnesium-salt. When the ash is poor in phosphoric acid, the addition of ammonia after the removal of the calcium does not precipitate all the magnesium: that which remains in solution must be precipitated by phosphate of sodium, or, if the alkalis are to be determined in the same solution, by phosphate of ammonium. When manganese is present, as well as iron and phosphoric acid, the phosphate of iron is first estimated, by saturation first with ammonia and then with acetic acid: the filtrate is then mixed with a known volume of a standard solution of ferric chloride (containing a known amount of iron) as neutral as possible, and the whole heated to boiling. The precipitate is washed with hot water, ignited, and weighed: it contains all the phosphorus and oxygen of the phosphoric acid, which is estimated by deducting from the weight of the precipitate that of the iron added as chloride. In the filtrate, manganese, calcium, and magnesium are determined as in 11.

For the estimation of the *alkaline metals*, the solution of the ash (after the separation of silica) is precipitated first by oxalate of ammonium, then by excess of ammonia, and finally (if necessary) by phosphate of ammonium. The precipitate having been thoroughly washed with water containing ammonia, the filtrate is somewhat evaporated to drive off free ammonia, and the phosphoric acid precipitated by acetate of lead: excess of lead is then removed from the unfiltered solution by carbonate of ammonium and ammonia, and the two precipitates filtered off together. The filtrate is evaporated to dryness, ignited to expel the ammoniacal salts, the residual alkaline chlorides weighed, and separated as in 8. *Iodine*, if present, is estimated in a separate portion of the ash by means of nitrate of palladium: the black precipitate, after standing for twelve hours, is collected on a weighed filter, dried over sulphuric acid, and weighed. (Pd I : I : : 180 : 127.) *Fluorine* is very rarely present: its quantity cannot be estimated.

If, as sometimes occurs in the case of graminaceous plants, the ash contains a silicate which is not decomposed by hydrochloric acid, it is best decomposed by hydrofluoric acid (26. b), and the silicon estimated by loss.

31. **Mineral Water.** (Mineral-springs, sea-water, spring-water.)

The following are the metals and acids which occur in mineral waters: —

Metals. — Potassium, sodium, ammonium, magnesium, calcium, iron, manganese, aluminium (rarely lithium, barium, strontium); also traces of copper, lead, tin, antimony, arsenic (and in some springs in mines, zinc).

Acids and Non-metallic Elements. — Carbonic (free and combined), hydrosulphuric (free and combined), silicic, sulphuric, phosphoric, boric (nitric), chlorine, bromine, iodine (fluorine); humic acids (crenic, and apocrenic), and occasionally volatile organic acids.

Those mineral waters which are poor in alkaline carbonates, and which contain the alkaline-earthy metals chiefly as chlorides and sulphates, scantily as acid carbonates, are called *saline* waters. Those which are rich in alkaline carbonates, and contain the alkaline-earthy metals as acid carbonates, are called *alkaline* waters. The latter are by far the richer in free carbonic acid, by which the normal alkaline-earthy carbonates are converted into acid carbonates, and so held in solution. Both these waters give a precipitate on boiling; the supernatant liquid of the saline waters is neutral, and generally contains soluble salts of calcium long boiling, and contains no soluble calcium- or magnesium-salts. Those waters which are rich in carbonate of iron are called *chalybeate:* those which contain soluble sulphides are called *sulphur-waters.*

In nearly every case a separate portion of the water should be taken for the determination of each constituent: for those which are present in very small proportion, a large quantity of water must be taken, and concentrated by evaporation to a small bulk. The first operation is to ascertain the *specific gravity.* This is done by means of a flask with a tightly-fitting perforated stopper, which is capable when filled with water of being closed so as to exclude any air-bubbles. The flask is weighed when empty, and again filled with distilled water at a known temperature: it is then emptied, dried (or rinsed out with the mineral water), filled with the mineral water at the same temperature, and again weighed; the weight of the mineral water divided by that of the distilled water gives the specific gravity of the former, that of the latter being taken as unity. The specific gravity being known, the portions of water for each determination can be measured off, since the weight of any given volume of water is readily calculated. (1 cubic centimetre of distilled water at 4° weighs 1 gramme.)

a. *Carbonic acid* is determined at the spring. A known volume of freshly drawn water is mixed in a stoppered flask with ammonia and chloride of barium: when the precipitate has quite subsided, the clear solution is passed through a filter, the precipitate washed two or three times with hot water by decantation, filtered without access of air, washed, dried at 100°, and weighed. If any of the precipitate cannot be washed out of the flask, it may be dissolved in dilute hydrochloric acid, reprecipitated by ammonia and carbonate of ammonium, and after washing, collected on the same filter. The precipitate thus obtained does not consist only of carbonate: it contains all the sulphuric acid in the water, as well as those substances which would be precipitated by boiling the water. The amount of carbonic acid in it must therefore be estimated by loss, as in 4. b. The amount thus obtained represents *all* the carbonic acid in the water, both free and combined. If another portion of the water be precipitated by boiling, and the amount of carbonic acid in the precipitate deducted from the total amount, the remainder will represent the amount of carbonic acid expelled by boiling: this however is not all free carbonic acid, since the acid carbonates are converted by boiling into normal carbonates. If the gas evolved by boiling the water be collected in a graduated tube over mercury, and the carbonic anhydride and hydrosulphuric acid absorbed by potash, the residual gas will indicate the amount of other gases (oxygen, nitrogen, and hydrocarbons) dissolved in the water.

b. *Hydrosulphuric acid* is determined at the spring. To a moderately large known volume of the water is added a little starch-solution, and then (from a burette) a standard solution of iodine in iodide of potassium (*see* No. 40), until the first appearance of a distinct blue colour. If the water is alkaline, it must be neutralised with acetic acid (or mixed with chloride of barium): if it is hot, it must be allowed to cool in a closed vessel. The decomposition of hydrosulphuric acid by iodine being expressed by the equation $I^2 + H^2S = 2HI + S$, the amount of hydrosulphuric acid present (free and combined) is readily calculated from that of iodine employed. ($I^2 : H^2S :: 127 : 17$.)

c. *The total weight of the fixed constituents* is ascertained by evaporating a known volume of water to dryness, heating the residue to about 150° or 200°, and weighing when cold. If much chloride of magnesium be present, an error will arise, as this salt is decomposed by heat: this may be prevented by dissolving in the water before evaporation a known weight of pure ignited carbonate of sodium.

d. *Chlorine* (*bromine and iodine*).—The water is acidulated with nitric acid and precipitated by nitrate of silver (3. a). Bromine and iodine are never present but in very small quantities, so that a very large volume of water must be taken for their determination. Iodine is precipitated by nitrate of palladium (30): bromine and chlorine together by nitrate of silver, and the weighed precipitate heated in a current of chlorine, and again weighed (p. 38).

e. *Sulphuric acid.*—The water is acidulated with hydrochloric acid, and precipitated by chloride of barium (1. c).

f. *Carbonates of iron, manganese, calcium, and magnesium:* perhaps *alumina.*—These are precipitated when the water is boiled for an hour in a flask. The precipitate is filtered off, dissolved in hydrochloric acid, and the different metals estimated as in 28. A large quantity of water should be employed for this determination.

g. *Silicon.*—A large quantity of water is acidulated with hydrochloric acid, evaporated to dryness, and the residue treated with dilute hydrochloric acid, when the silica alone remains insoluble, and is dried, ignited, and weighed. Should the residue contain sulphate of calcium, a considerable quantity of water will be required to dissolve it.

h. *Boric acid.*—The water is mixed with carbonate of sodium, concentrated by evaporation, and acidulated with hydrochloric acid: turmeric paper dipped into it becomes brown when dried, if boric acid be present.

i. *Potassium and sodium.*—The water is boiled in a flask to about half its volume, and, without filtering, mixed with excess of baryta-water, and filtered. Excess of barium is removed from the filtrate by carbonate of ammonium and ammonia: the filtrate is evaporated to dryness (with addition of chloride of ammonium if the alkaline metals are not present as chlorides), the residue gently ignited and treated as in 8.

k. *Carbonate of sodium* (in alkaline waters).—The water is boiled for an hour, filtered, and the filtrate divided into two equal parts. In one, acidulated with nitric acid, the chlorine is precipitated by nitrate of silver. The other is acidulated with hydrochloric acid, evaporated to dryness, the residue gently ignited and redissolved in water, and the solution precipitated by nitrate of silver. The difference between the weights of this portion of chloride of silver and the former, corresponds to the amount of carbonate of sodium in the water. ($2AgCl : CO^3Na^2 :: 287 : 106.$)

l. *Calcium and magnesium,* (as soluble salts in saline waters).—Calcium is precipitated from the boiled and filtered water by oxalate of ammonium (4): magnesium from the filtrate by phosphate of sodium (5).

m. If *lithium* be present, it remains with the other alkaline chlorides when the water is treated as in (i). The three chlorides are dissolved in water, the potassium precipitated as chloroplatinate, the filtrate (freed from platinum) evaporated to dryness, and the residue treated with alcohol and ether, which dissolves the chloride of lithium only. For the estimation of *ammonium*, a large quantity of water is acidulated with hydrochloric acid, evaporated to dryness but not ignited, the residue boiled with potash, and the ammonia evolved collected in dilute hydrochloric acid (p. 191). *Nitric acid* is of rare occurrence: it is detected in the concentrated water by ferrous sulphate; but its estimation is very difficult. Perhaps it may be effected by distilling the concentrated water, after removing the chlorine by sulphate of silver, with sulphuric acid, and saturating the distillate with baryta-water (p. 9).

n. *Strontium*, *barium*, *aluminium*, *manganese*, *phosphoric acid*, and *fluorine*, are to be sought for in the deposit which forms in many mineral waters by boiling or exposure to the air. *Copper*, *lead*, *tin*, *antimony*, and *arsenic* are to be sought in the same deposit, which is dissolved in hydrochloric acid, and treated with hydrosulphuric acid: Marsh's apparatus may be employed to detect the two latter metals.

o. *Organic matter.* — When organic matter is present, the residue obtained by evaporating the water to dryness blackens when strongly heated. The total amount cannot be accurately estimated by heating till the carbon is entirely burnt: for some of the inorganic constituents would be decomposed by the heat. The deposit formed in the water by boiling sometimes contains peculiar organic acids, *crenic* and *apocrenic* acids. They are separated by boiling the deposit with potash for many hours, saturating the solution with acetic acid, and adding acetate of copper, which precipitates the apocrenic acid: the crenic acid is precipitated by heating the filtrate with carbonate of sodium. Volatile organic acids (*formic*, *acetic*, *propionic*, &c.) are separated by distilling the concentrated water (after removal of chlorine &c.) with strong sulphuric acid.

32. **Estimation of Carbonic Acid.** (Applied to the valuation of commercial potash and soda, of acids, and of binoxide of manganese.)

All carbonates are decomposed by strong acids; the carbonic acid which is liberated splits up into water and carbonic anhydride (CO^2), which latter escapes in the gaseous form. If the weight of the carbonic anhydride evolved is known, the weight of carbonic acid to which it corresponds is readily calculated. It is on this principle that the amount of carbonate present in any solid compound is usually estimated. The apparatus employed consists of a small light flask fitted with a cork perforated with two holes: into one of these is fitted a tube filled with fragments of chloride of calcium; into the other a narrow tube reaching almost to the surface of the liquid in the flask, and bent above the cork at a right angle. A weighed portion of the dry substance is introduced into the flask, which is then filled about one-third with water: a small tube of such a length as to lean against the side of the flask, containing enough sulphuric* acid to decompose all the carbonate, is placed in the flask: the cork with its tubes attached is then fitted air-tight into the flask, and the whole apparatus weighed. The orifice of the bent tube is then closed with a plug of cork or wax, and the apparatus inclined so that a small portion of the acid flows from the tube into the solution in the flask: when the effervescence has subsided, a fresh portion of acid is allowed to escape; and so on till the carbonate is entirely decomposed. The carbonic anhydride evolved escapes through the chloride of calcium tube, which retains any moisture that may be carried with it. When the effervescence has entirely ceased, the plug is removed from the bent tube, and suction applied to the chloride of calcium tube until all the carbonic anhydride in the flask is replaced by air: the whole is again weighed, when the loss of weight indicates the amount of carbonic anhydride that has escaped. The carbonic anhydride dissolved in the liquid in the flask must be expelled by heat before weighing the flask.

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* Nitric acid must be used to decompose the carbonates of barium, calcium, or lead.

a. *Alkalimetry.*—It is obvious that this process may be applied to the valuation of commercial carbonates of potassium and sodium (commonly called potash and soda), the value of which depends entirely on the amount of real carbonate they contain. The impurities in potash are generally chloride, sulphate, silicate, and phosphate of potassium, carbonate, silicate, and phosphate of calcium: those in soda are chloride, sulphide, sulphate, hyposulphite, silicate, and hydrate of sodium. The amount of water in the sample is ascertained by heating it to about 200°, and weighing: the dry sample is then decomposed in the above apparatus. The proportion for the potash sample is $CO^2 : CO^3K^2 :: 22 : 69$; for the soda, $CO^2 : CO^3Na^2 :: 22 : 53$. If the soda sample contain any caustic soda, which is known (in the absence of sulphide) by its solution having an alkaline reaction after the addition of excess of chloride of barium, another equal portion must be mixed with about 3 parts of pure quartz-sand and about $\frac{1}{3}$ part carbonate of ammonium, moistened with water, and heated till the water and ammonia are expelled: the dry residue is then decomposed as above. The excess of sodic carbonate obtained in the second determination, is due to the caustic soda in the sample: from it the amount of the latter is easily calculated. ($CO^3Na^2 : 2NaHO :: 106 : 80$.) If it contains any sulphide or hyposulphite, these salts must be oxidised by the addition of some chromate of potassium to the solution in the flask, before commencing the decomposition.

b. *Acidimetry.* —Another purpose to which this process may be applied is that of determining the amount of real acid contained in commercial acids. This is done by decomposing an excess of pure acid carbonate of sodium by a known weight of the acid to be valued: as the decomposition takes place atom for atom, the amount of real acid present is readily calculated from the weight of carbonic anhydride evolved. The following will serve as examples of the mode of calculation:

Sulphuric acid - $(2CO^3NaH + SO^4H^2 = SO^4Na^2 + 2CO^2 + 2H^2O)$
$2CO^2 : SO^4H^2 :: 44 : 49.$

Hydrochloric acid - $(CO^3NaH + ClH = ClNa + CO^2 + H^2O)$
$CO^2 : ClH :: 44 : 36{\cdot}5.$

Acetic acid - $(CO^3NaH + C^2H^3O^2H = C^2H^3O^2Na + CO^2 + H^2O)$
$CO^2 : C^2H^3O^2H :: 44 : 60.$

c. *Valuation of Manganese-ores.*—Binoxide of manganese is decomposed by oxalic acid in presence of sulphuric acid, giving up half its oxygen to the oxalic acid, which is thereby converted into carbonic anhydride and water ($Mn^2O^2 + C^2O^4H^2 = Mn^2O + 2CO^2 + H^2O$): 2 molecules of carbonic anhydride being formed for each molecule of binoxide. Hence the amount of binoxide of manganese contained in commercial manganese-ore is readily estimated by the aid of the carbonic-acid apparatus. The moisture in the ore is first determined by heating it to 100°—120°. A weighed portion of the dry ore is then introduced into the flask, with about twice its weight of normal oxalate of potassium; water is then added, and the decomposition effected as above by an excess of concentrated sulphuric acid. From the weight of carbonic anhydride evolved, the amount of binoxide of manganese is readily calculated. ($2CO^2 : Mn^2O^2 :: 44 : 42.$) Good manganese-ore is crystalline in texture, and yields a black powder: after having been dried, it should scarcely lose weight when heated to dull redness.

33. **Earthy Phosphates.** (Sesquiphosphates of iron and aluminium, phosphates of magnesium and calcium.)—Fownes.

These phosphates are frequently met with together in the analysis of ashes of plants. They are all soluble in hydrochloric acid, and are reprecipitated unchanged by ammonia: when freshly precipitated, the phosphates of calcium and magnesium are soluble in warm acetic acid; those of iron and aluminium are not. Phosphate of aluminium closely resembles hydrate of aluminium both in appearance and properties, being soluble in potash, whence it is precipitated by chloride of ammonium. Basic phosphate of iron also closely resembles sesquihydrate of iron in colour and general appearance. When sufficient tartaric acid is added to the hydrochloric acid solution of these two phosphates, they are not precipitated by excess of ammonia: on adding sulphate of magnesium to the alkaline solution, crystalline phosphate of magnesium and ammonium is precipitated, insoluble in chloride of ammonium.

Qualitative analysis.—First ascertain whether any soluble matter be present, by boiling the powdered substance in water, and examining the solution. Dissolve in hydrochloric acid, add ammonia in slight excess, and filter: after thoroughly washing the precipitated phosphates, digest them in warm acetic acid, and filter off the insoluble residue. Examine the residue for aluminium by potash and chloride of ammonium, and for iron by sulphide of ammonium. From the acetic acid solution, precipitate the calcium by oxalate of ammonium: on saturating the filtrate with ammonia, the magnesium is precipitated as phosphate. The solution still contains phosphoric acid, which is precipitated by adding sulphate of magnesium and chloride of ammonium. If the mixed phosphates contained any carbonate, a soluble calcium- or magnesium-salt will be found in the solution from which the phosphates were precipitated by ammonia.

Quantitative analysis.—The freshly precipitated phosphates are digested in warm acetic acid, and filtered: too much heat must be avoided; the filtration is usually slow and difficult. From the solution, which contains all the calcium and magnesium, the calcium is precipitated as oxalate, filtered off, dried, ignited, and weighed (4. a). The filtrate is then saturated with ammonia, when the magnesium is precipitated as double phosphate, which is ignited and weighed (5. a). In order to determine the phosphoric acid in the filtrate from the magnesium-salt, it is mixed with a solution in aqua-regia of a known weight of pure iron, and a slight excess of ammonia added: the precipitated ferric hydrate carries down with it all the phosphoric acid, the amount of which is calculated from the increase in weight of the dried and ignited precipitate over that of the amount of ferric oxide which corresponds to the weight of iron employed (*see* 6). 7 parts iron correspond to 10 parts ferric oxide. This method is not accurate if the weight of ferric oxide be less than 4 times that of phosphoric acid.

The residue insoluble in acetic acid, which contains the phosphates of iron and aluminium, is dissolved in hydrochloric acid, and boiled with sulphurous acid and excess of caustic soda till all the iron is precipitated as black ferroso-ferric oxide, which is filtered off, dissolved in aqua-regia, and precipitated by ammonia (2. a). The alkaline filtrate is diluted, mixed with chloride of barium and carbonate of sodium, and boiled, when all the phosphoric acid is precipitated as phosphate of barium: this is filtered off, dissolved in hydrochloric acid, the barium precipitated by sulphuric acid, and the phosphoric acid determined in the filtrate as phosphate of magnesium and ammonium (6. a). The filtrate from the phosphate of barium is acidulated with hydrochloric acid, and the aluminium precipitated by sulphide of ammonium (23).

34. **Platinum-ores and Platinum-residues.**

Platinum-ore contains 74—86 p. c. platinum, besides iridium, palladium, rhodium, osmium, ruthenium, iron, and copper: it is mixed with grains of osmide of iridium, magnetic, titanic, and chrome-iron, gold, &c. The accurate quantitative analysis of this ore is very difficult: it is probable that the methods here given are only approximative.

a. The ore is purified as far as possible by picking out the dark steel-coloured grains of osmide of iridium, and removing the magnetic grains with a magnet. About 10 grm. are then digested in a retort, with aqua-regia containing 5 parts fuming hydrochloric acid, and 1 part fuming nitric acid: a cooled receiver is attached, and distillation continued, the distillate being poured back once or twice, as long as anything is dissolved. The distillate contains most of the *osmium* as osmic acid. The solution in the retort is poured off from the residue, which is washed, dried, weighed, and analysed as in b.

The solution contains all the *palladium*, most of the *platinum*, some *osmium*, *rhodium*, *iridium* (copper and iron). It is mixed with twice its bulk of alcohol, and then with a warm saturated solution of chloride of potassium, till no farther precipitate is formed: the precipitate is filtered off, and washed with alcohol containing chloride of potassium.

The *precipitate* contains chloroplatinate and chloriridate of potassium (together with osmium and traces of rhodium and palladium): the presence of iridium gives it a reddish colour. It is intimately mixed with an equal weight of carbonate of sodium, and gently ignited (together with the filter-ash) in a porcelain crucible until the whole mass is black: the platinum is thus reduced, the iridium and osmium oxidised. The black mass is exhausted with water and hydrochloric acid, which remove the osmate of potassium and excess of carbonate: the former may be added to the distillate containing osmic acid. The residue is dried, ignited, and weighed: it is then fused for some time with 6 parts acid sulphate of potassium, by which all the *rhodium* is converted into a soluble salt, which is extracted with water; the residue is again weighed, and the *rhodium* determined by loss. The mixture of platinum and sesquioxide of iridium is then digested, in very dilute aqua-regia, which extracts part of the platinum: the clear solution is poured off, saturated with ammonia, evaporated to dryness, and ignited, when pure *platinum* remains. The rest of the platinum, together with the sesquioxide of iridium, is mixed with chloride of sodium and concentrated aqua-regia, and evaporated to dryness: exhaustion with water removes the *platinum-salt*, and the *oxide of iridium* is left. This is washed with chloride of sodium, and finally with chloride of ammonium, ignited, reduced by hydrogen, and weighed as metallic *iridium*. The platinum solution still contains some iridium, so that this process must be repeated.

The *filtrate* contains rhodium, palladium, some iridium, iron, and copper. It is evaporated to dryness, and the residue digested with strong aqua-regia, chloride of potassium added, and the whole again evaporated to dryness. Digestion with alcohol removes the chlorides of *copper* and *iron*, leaving the double salts of palladium, rhodium, and iridium. These are fused with bichromate of potassium, and the mass treated with water, when the *iridium* is left as sesquioxide. From the solution neutralised by carbonate of sodium, *palladium* is precipitated by cyanide o mercury; the precipitate on ignition leaves the metal. The filtrate is boiled with hydrochloric acid till it becomes red, and the *rhodium* precipitated as hydrate by potash.

The distillate, containing all the *osmium* as osmic acid is neutralised with lime, and heated with an alkaline formate, which reduces the osmium as a bluish-black powder. Or it is mixed with ammonia and chloride of ammonium, evaporated to dryness in a retort, and ignited till only metallic osmium remains. Or it is saturated with potash, and heated with alcohol, when osmite of potassium separates, whence metallic osmium may be obtained (p. 139). (Wöhler.)

b. The portion of platinum-ore which is insoluble in aqua-regia is generally called *platinum-residues.* It contains *osmide of iridium*, *iridium* (in powder), *ruthenium*, traces of *rhodium*, *platinum*, and (sometimes) gold, magnetic, titanic, and chrome-iron- ores, silicates, &c. It is fused in a silver or wrought-iron crucible for an hour at a red heat, with 2 parts nitre and 1 part caustic potash, and the mass when cool digested with cold water in a stoppered bottle. After 12 hours the clear orange-coloured solution is poured off from the black residue.

The *solution* which contains osmate and ruthenate of potassium is mixed with nitric acid, and the precipitated ruthenic oxide freed from osmium by distillation with aqua-regia. The solution is freed from osmium in the same manner, and is then evaporated with hydrochloric acid, when nitre crystallises out first, and then rose-red chlororuthenate of potassium, whence metallic *ruthenium* is obtained.

The *residue*, which may contain all the platinum-metals as oxides, is freed from *osmium* by distillation with aqua-regia, when some impure oxide of rhodium often remains undissolved. The solution is evaporated, and precipitated by chloride of ammonium: the double salts of the platinum-metals are filtered off, and washed with chloride of ammonium till the wash-water passes through colourless. The solution contains the *iron*, *copper*, and *chromium.* By prolonged digestion of the double salts in cold water the chlororuthenate is dissolved out first; from the solution the oxide is precipitated by heating with ammonia, and this is reduced by hydrogen to metallic *ruthenium.* The chloroplatinate and chloriridate are digested with water containing hydrosulphuric or sulphurous acid, which reduces the iridium to sesquichloride: the solution is evaporated, and, without filtering, mixed with chloride of ammonium. The precipitated chloroplatinate on ignition leaves metallic *platinum:* the solution is evaporated to dryness, and the residue, ignited in a stream of hydrogen, leaves metallic *iridium.*

Gold, if present, may be precipitated by oxalic acid.

Fremy (Compt. rend. xxxviii. 1008) gives the following simpler method of treating platinum-residues, which seems to be particularly adapted for obtaining the metals in a state of purity. About 200 grm. of the residues are heated to bright redness in a long porcelain tube, purified air being drawn over the heated ore by means of an aspirator. *Osmium* and *ruthenium* combine with oxygen: ruthenic oxide crystallises in the cold part of the tube in violet crystals; while the more volatile osmic acid passes first into a series of empty tubes, in which a part is deposited in crystals, and finally into a solution of potash. An alloy of *iridium* and *rhodium* remains in the roasting tube. This is calcined in an earthen crucible, with 4 parts nitre, care being taken not to carry the operation too far, exhausted with water, and filtered: the alkaline filtrate on evaporation deposits crystals of osmite of potassium, the osmium not being entirely removed by the roasting. The precipitate on the filter, which contains potash, is treated for several hours with aqua-regia, which converts the *iridium* into chloriridate of potassium, nearly insoluble in cold water. It is dissolved by boiling water, the washing being continued as long as the wash-water has a brown colour; and the chloriridate crystallises on evaporating the solution. The residue, containing the *rhodium,* is dried, mixed with an equal weight of chloride of sodium, and treated for 3 or 4 hours by dry chlorine at a red heat. Chlororhodate of sodium is thus formed, which by solution in water and evaporation, is obtained in fine rose-coloured crystals. (Graham's Chemistry, ii. 418).

35. **Ferrocyanide of Potassium.** ($Cy^6Fe^2K^4 + 3H^2O$.)

a. The *water* is determined by heating the salt to 200°.

b. The *cyanogen* can only be estimated directly by combustion with oxide of copper.

c. *Iron and Potassium.*—The salt is dissolved in water, and the solution precipitated by acetate of lead. The ferrocyanide of lead is filtered off, washed, and decomposed by digestion with sulphide of ammonium; the sulphide of lead filtered off and washed; the filtrate (of ferrocyanide of ammonium) evaporated to dryness, the residue ignited in the air till pure ferric oxide is left, which is weighed (2). From the original filtrate the excess of lead is removed by hydrosulphuric acid, the solution evaporated to dryness, and the residue converted by ignition into carbonate of potassium, which is converted into sulphate, and weighed (3). ($SO^4K^2 : K^2 :: 87 : 39$.)

Or the salt may be fused with acid sulphate of ammonium, the ignited residue of ferric oxide and potassic sulphate dissolved in hydrochloric acid, the iron precipitated by ammonia, the solution evaporated to dryness, and the residual potassic sulphate weighed.

To estimate the iron alone, the salt is fused with 3 parts of a mixture of nitre and carbonate of sodium in a platinum crucible. On treating the fused mass with water, the iron is left as sesquioxide: as this contains some potash, it must be dissolved in hydrochloric acid, and precipitated by ammonia. (Wöhler.)

Section II. Volumetric Analysis.

The methods of estimating substances which have been hitherto described depend upon the separation of the substance in a form in which it can be weighed directly; or upon its conversion into a compound which is capable of being weighed, the weight of which bears a known proportion to that of the substance to be estimated: the reagent by which the separation is effected being always employed *in excess.* The methods of estimation in the wet way, which are included under the general name of Volumetric Analysis, depend, on the contrary, 1, upon the employment of only the exact amount of the reagent which is necessary to produce the reaction desired; 2, upon the determination of this amount, not by weight, but by measure, which is effected by the employment of solutions which in a known volume contain a known weight of the reagent. These solutions are called *Standard Solutions.* The volumetric method of analysis is only applicable in cases where the point at which the reaction is complete can be determined with certainty by means of some phenomenon which is manifested in the solution of the substance to be estimated, *i.e.* by an appearance, disappearance, or change, of colour, or by the appearance or disappearance of a precipitate.

The unit of volume ordinarily adopted is the cubic centimetre (c.c.), which is the volume occupied by 1 gramme of water at 4°. The vessels employed for measuring volumes are, for large quantities, graduated cylinders, or flasks whose volume is known and marked on the outside: for small quantities, *pipettes* and *burettes,* which are graduated into cubic centimetres and fractions of the c.c. By far the most convenient form of burette for general purposes is that devised by Mohr, which discharges the liquid from its lower extremity, the discharge being regulated by means of a pinchcock, and a caoutchouc tube.

When the reagent is a stable compound, and not liable to decomposition by keeping, a standard solution of it is prepared once for all, and kept in a stoppered bottle ready for use. In the case of compounds that are easily decomposed, a moderately concentrated solution is prepared, and its value (or standard) is ascertained on each occasion previous to its employment.

There are two methods of estimation by volumetric analysis: 1, the *direct* method; 2, the *indirect,* or *residual* method. The first is employed when the point at which the reaction between the reagent and the substance to be estimated is complete, can be exactly ascertained by one of the phenomena indicated above; in such cases the necessary amount of the reagent is measured off directly. The second is employed when the point of complete reaction cannot be exactly ascertained. It is then necessary to employ a second reagent between which and the first the point of complete reaction is capable of being determined. A known volume of the first reagent, more than is needed for the complete reaction, is added to the solution of the substance to be estimated: and the excess of the first reagent is then ascertained by means of the second.

36. **Alkalimetry**. (Estimation of the amount of alkali or alkaline carbonate in commercial potash, soda, or ammonia.)

This estimation depends upon the facts that the alkaline salts of strong acids (oxalic, sulphuric, &c.) are neutral to litmus; and that the violet solution of litmus is coloured blue by caustic alkalis or alkaline carbonates, wine-red by carbonic acid, and light-red by strong acids.

a. *Direct method.*—A standard acid solution is the only one required. Oxalic acid is the most convenient acid for this purpose; for it can be weighed with greater accuracy than any liquid acid, and its solution can be kept for any length of time without undergoing any change. It is best to make the standard solution of such strength that 1000 c.c. (1 litre) shall contain exactly one $\frac{1}{2}$-*gramme-atom* (*i.e.* 1 atom expressed in $\frac{1}{2}$ grammes) of the acid. This is done by dissolving in water $\frac{126}{2}=63$ grammes of pure crystallised oxalic acid ($C^2O^4H^2+2H^2O=126$), and diluting the solution to the bulk of 1 litre, at 17·5°. 1000 c.c. of this solution contains 1 $\frac{1}{2}$-gramme-atom of acid: hence 2 c.c. contain 1 milligramme-atom of acid, and saturate 2 milligramme-atoms of a caustic alkali or 1 milligramme-atom of an alkaline carbonate.

Since pure oxalic acid cannot be always readily obtained, sulphuric acid may be employed for the standard solution. About 70 grm. concentrated sulphuric acid are diluted with about 600 grm. water: when the mixture is cool, the volume of it that is necessary to saturate 5·3 grm. (1 $\frac{1}{2}$-decigramme-atom) pure anhydrous carbonate of sodium is determined. 5·3 grm. freshly ignited carbonate of sodium are dissolved in hot water, the solution coloured blue with a few drops of litmus, and the acid added from a burette (at last drop by drop) till the colour just passes from wine-red to light-red, and till strips of litmus-paper, moistened with the solution, begin to retain the red colour when dry. The volume of acid employed is then noted, and the whole diluted so as to approximate to the required strength. Suppose, for instance, 37 c.c. acid have been used: water is added till every 100 vols. is diluted to 250 vols. and another determination made. If 90 c.c. are now required to saturate the ½-decigramme alkaline solution, every 90 vols. of the acid must be diluted to 100, and the result controlled by a fresh determination. 100 c.c. of this acid should exactly saturate 5·3 grm. carbonate of sodium, and will contain 1 ½-decigramme-atom of acid: 2 c.c. will contain 1 milligramme-atom (·098 grm.) sulphuric acid, and will exactly saturate 2 milligramme-atoms of an alkali or 1 milligramme-atom of an alkaline carbonate. The standard solution is kept in a well-stoppered bottle.

A weighed portion of the substance to be estimated is dissolved in water (if a solid), a few drops of litmus added, and the standard acid added from a burette until the first permanent appearance of a light-red colour: and the volume of acid employed is read off. Each c.c. of acid corresponds to 1 milligramme-atom of alkali or 1 ½-milligramme-atom of alkaline carbonate; *i. e.* to 0·053 grm. carb. sod., 0·069 grm. carb. pot., 0·040 grm. caustic soda, 0·056 grm. caustic potash, 0·017 grm. ammonia: and a simple proportion gives the amount of alkali or alkaline carbonate (*e. g.* 100 : 6·9 : : number of c.c. employed : carbonate of potassium present). By operating on 100 times the ½-milligramme-atom (*e. g.* 6·9 grm. in the case of potassic carbonate, 5·3 grm. in the case of sodic carbonate), all calculation is saved: for as this amount, if perfectly pure, would require 100 c.c. acid for its saturation, the number of c.c. actually required at once indicates the percentage of alkaline carbonate. The burettes commonly used contain 50 c.c., and are graduated into half c.c.; so that by operating on 50 times the ½-milligramme-atom, the number of divisions employed represents the percentage.

b. *Residual method.* — The standard acid is added until the colour of the litmus is a distinct light-red; the solution is then heated to boiling, and a small excess of acid (5—10 c.c.) added. The hot solution is freed from carbonic acid by agitation and by drawing air through it by means of a glass tube; and then neutralised with a standard alkaline solution (37) until the colour just changes from red to blue. Since the acid and alkaline solutions neutralise each other volume for volume, it is only necessary to deduct the number of c.c. employed of the latter from that of the former, and to calculate the amount of alkali from the residue. This method is preferable for the estimation of carbonates, since the change from blue to red is more distinctly marked than that from one shade of red to another.

37. **Acidimetry.** This estimation depends on the same principles as the preceding.

The most convenient alkaline solution is caustic soda (perfectly free from carbonate); it is standardised so that 100 c.c. exactly saturate 100 c.c. of the standard acid solution. It is kept in a flask into the cork of which is inserted a chloride of calcium tube filled with a mixture of Glauber's salt and caustic lime, which effectually prevents the absorption of carbonic acid. If the burette be closed with a similar tube, the soda-solution may remain in it for days. The estimation is performed precisely as in 36, the last drops of the soda-solution being added from a pipette graduated to $\frac{1}{10}$ c.c. Since the normal alkaline salts of strong acids are perfectly neutral, the exact point of saturation is attained when the litmus is restored to its original colour. The best method of observing this with precision is to colour a certain quantity of pure water with litmus, and to divide it into two equal portions: the acid is added to one, while the other is kept at hand as a standard of comparison. Calculation may be avoided, as above, by operating on a weight of acid equal to 50 (or 100) times its $\frac{1}{2}$-milligramme-atom. When several (*e. g.* 5) estimations of the same acid have to be made, the readiest method is to weigh out 500 times the $\frac{1}{2}$ milligramme-atom of the acid (*e. g.* $5 \times 4{\cdot}9$ grm. sulphuric acid), to dilute it to 250 c.c., and to take 50 c.c. of the mixture for each determination: the number of c.c. soda-solution employed represents the percentage of acid.

38. **Chlorimetry.** (Valuation of chloride of lime.)

Chloride of lime (bleaching powder) contains hypochlorite, chloride, and hydrate of calcium in varying proportions. Its value depends upon the amount of hypochlorite which it contains, or upon the quantity of chlorine which it evolves when treated with acids. It is the estimation of this chlorine which constitutes chlorimetry.

a. The amount of the substance which is necessary to oxidise a known weight of arsenious anhydride in an *acid* solution, is estimated directly. Free chlorine, in presence of water, converts arsenious into arsenic anhydride, hydrochloric acid being formed at the same time ($As^2O^3 + Cl^4 + 2H^2O = As^2O^5 + 4ClH$). If indigo be present in the arsenious solution, it is not acted upon by the chlorine until the oxidation of the arsenic acid is completed; the disappearance, therefore, of the blue colour marks the end of the operation.

Standard solution.—14 grm. pure arsenious anhydride, dried at 100°, are dissolved in caustic potash, and the solution diluted to 1 litre. 1 c.c. of this solution contains 0·014 grm. arsenious anhydride, and requires for its conversion into arsenic anhydride 0·010 grm. chlorine. ($As^2O^3 = 198 : Cl^4 = 142 :: 14 : 10$.)

5 grm. chloride of lime are triturated with water, the whole washed into a graduated cylinder, and diluted to 100 c.c. 50 c.c. arsenious solution are placed in a beaker, diluted with water, saturated with hydrochloric acid, and coloured blue with a drop of indigo-solution: the solution of chloride of lime (which should be well shaken up) is then added from a burette, until the blue colour is nearly destroyed. A fresh drop of indigo is then added; and then the chloride-solution again, very cautiously and drop by drop, the contents of the beaker being continually agitated, until the colour finally disappears. The amount of chlorine contained in the volume of chloride-solution (or weight of chloride of lime) employed, is 0·5 grm., that being the quantity necessary to oxidise 50 c.c. of the standard solution. For instance, suppose 45 c.c. chloride-solution have been employed: 5 grm. bleaching powder will contain 1·1 grm. chlorine; and the percentage of available chlorine in the sample is 22·2 p.c. 1000 c.c. chlorine, at 0° and 760 mm. pressure, weigh 3·1884 grm.

b. The substance is made to react on a known volume of a standard *alkaline* solution of arsenious anhydride, which is employed in excess: and the excess is estimated by a standard solution of iodine (40. c). According to Mohr, this is the only accurate method.

c. The substance is made to react on a known weight of a ferrous salt, which is added in excess: and the excess is estimated by a standard solution of permanganate of potassium (45).

39. **Valuation of Manganese-ores.** (Determination of the amount of available oxygen which they contain.)

a. *By chlorimetry.*—Binoxide of manganese, heated with hydrochloric acid, evolves chlorine, in the proportion of 2 atoms chlorine for each atom of binoxide ($Mn^2O^2 + 4ClH = 2MnCl + 2H^2O + Cl^2$). The ore (the moisture in which is first estimated) is heated in a flask with excess of concentrated hydrochloric acid, and all the chlorine evolved conducted into a dilute solution of soda, into milk of lime, into a known volume of the standard acid or alkaline arsenious solution, or into excess of iodide of potassium; and the amount of chlorine estimated by one of the chlorimetrical processes (38). The amount of binoxide of manganese corresponding to a given weight of chlorine is easily calculated. ($Cl^2 : Mn^2O^2 :: 71 : 84$).

Each c.c. of the acid arsenious solution (37. a) corresponds to 0·010 grm. chlorine, and to 0·01183 grm. binoxide: hence 50 c.c. correspond to 0·5 grm. chlorine, and to 0·5915 binoxide. If the ore be rich, about 1 grm is sufficient for analysis: if it be poor, 1·5—2 grm. should be taken.

Each c.c. of the alkaline arsenious solution (40) corresponds to 0·00355 grm. chlorine, and to 0·0042 grm. binoxide: hence 100 c.c. correspond to 0·42 grm. binoxide; and if 0·42 grm. ore be taken for analysis, the number of c.c. of arsenious solution which is oxidised by it gives at once the percentage of binoxide.

b. *By oxalic acid and cameleon* (permanganate of potassium). —A dilute solution of oxalic acid decomposes permanganates in presence of sulphuric acid, being itself converted into carbonic anhydride and water ($Mn^4O^8H^2 + 2SO^4H^2 + 5C^2O^4H^2 = 2SO^4Mn^2 + 8H^2O + 10CO^2$). Under the same circumstances oxalic acid decomposes binoxide of manganese, atom for atom ($Mn^2O^2 + SO^4H^2 + C^2O^4H^2 = SO^4Mn^2 + 2H^2O + 2CO^2$). Hence the amount of binoxide of manganese in an ore can be estimated volumetrically, by allowing it to react upon a known volume of a standard solution of oxalic acid, which is added in excess, and then estimating the amount of undecomposed oxalic acid by a standard solution of cameleon.

The standard solutions required are:

1. *Oxalic acid.*—This is the same as that employed for alkalimetry. 1 c.c. contains 0·063 grm. crystallised oxalic acid, and corresponds to 0·042 grm. binoxide.

2. *Cameleon.*—Since this solution cannot be preserved without decomposition, it is not standardised once for all; but a moderately strong solution is prepared, and its exact value determined before each operation. This is readily done by means of the standard solution of oxalic acid. 5 c.c. of the latter are diluted to 200 c.c., about 4 c.c. strong sulphuric acid are added, and the cameleon-solution introduced, drop by drop, from a burette.* The dark colour produced by the cameleon disappears at first slowly, but more rapidly as the operation proceeds: the operation is terminated when a faint rose-tinge is produced which remains permanent for a short time. Suppose, for instance, 29 c.c. cameleon-solution are employed: 1 c.c. cameleon corresponds to $\frac{5}{29} = 0{\cdot}1724$ c.c. oxalic acid.

The analysis is conducted as follows.—The ore having been finely powdered and completely dried, 2·1 grm. are treated with about 30 c.c. standard oxalic acid, and 4 c.c. concentrated sulphuric acid: when the evolution of carbonic anhydride slackens, heat is applied, till no more gas is evolved. If any of the ore remains undecomposed, 5 or 10 c.c. more oxalic acid must be added. When the evolution of gas has quite ceased, the clear solution is decanted into a graduated cylinder, and the residue is treated with 2 or 3 c.c. more oxalic acid, and a few drops of sulphuric acid, and again heated. When the decomposition is complete, the solution (residue and all) is washed into the cylinder, and the whole diluted to a known volume. The mixture thus obtained is never clear; but it need not be filtered unless it is dark-coloured. A known volume of it is measured off, diluted, acidulated with sulphuric acid, and the amount of non-oxidised oxalic acid estimated by the cameleon-solution, as above: from the result thus obtained, the amount of non-oxidised oxalic acid in the whole mixture is calculated. The number of c.c. of oxalic acid oxidised, multiplied by 2, gives the percentage of binoxide in the ore.

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* The burette above alluded to, which discharges the liquid through a caoutchouc tube, cannot be used for cameleon, since this substance is reduced by any organic matter. Cameleon-solution is best kept in a flask fitted with tubes like a wash-bottle: it may thus be transferred to the burette without exposing the contents of the flask to dust or other impurities, and without disturbing any sediment that may have formed in the flask. Moreover the solution never touches the cork. According to Mohr, cameleon may be preserved for months in this manner, without any sensible variation in its standard.

Example.—1 c.c. cameleon = 0·1724 standard oxalic acid. Weight of ore taken, 2·1 grm. Total volume of oxalic acid used, 48 c.c. The mixture being diluted to 300 c.c., 100 cc. require 4 c.c. cameleon: hence the whole 300 c.c. require 12 c.c. cameleon, which correspond to 2·07 c.c. oxalic acid. 48 − 2·07 = 45·93 c.c. oxalic acid oxidised by binoxide: whence percentage of binoxide is 45·93 × 2 = 91·86 p. c.

If, instead of 2·1 grm., any arbitrary weight of ore is taken, the amount of binoxide is calculated by the proportion 100 : 4·2 : : number of c.c. oxalic acid oxidised : amount required; the percentage is then calculated as usual.

40. Volumetric determinations by Iodine and Arsenious anhydride.

Arsenious anhydride in an *alkaline* (not in an aqueous or acid) solution, is completely oxidised by iodine in presence of water, and converted into arsenic anhydride, hydriodic acid being simultaneously produced: enough alkali must be present to saturate the hydriodic acid formed. ($As^2O^3 + I^4 + 2H^2O = As^2O^5 + 4IH.$) The blue colour of iodide of starch is destroyed by the alkaline arsenious solution: if therefore starch-paste be added to the latter, and an iodine-solution gradually mixed with it, the blue colour will appear at the moment when the arsenious anhydride is completely oxidised.

Hence arsenious anhydride may be estimated volumetrically by means of an iodine solution of known strength; and reciprocally iodine may be determined by means of a standard solution of arsenious anhydride. And if any substance which oxidises or precipitates the arsenious solution be allowed to react completely upon an excess of that solution, the volume employed being known, the amount of arsenious anhydride oxidised or precipitated by the substance can be estimated by means of a standard solution of iodine.

The standard solutions required are:

1. *An arsenious solution.* — 4·95 grm. ($\frac{1}{40}$ gramme-atom) pure and dry arsenious anhydride are dissolved by heating with about 15 grm. acid carbonate of sodium, and the solution diluted to 1000 c.c. 1 c.c. contains 0·00495 grm. arsenious anhydride.

2. *An iodine-solution.*— 12·7 grm. ($\frac{1}{10}$ gramme-atom) iodine are dissolved in iodide of potassium, and the solution diluted to 1000 c.c. Iodine is seldom quite free from chlorine; and even if pure iodine be employed, the solution cannot be kept without a lowering of its standard. Hence the real amount of iodine contained in it must be determined before each experiment. For this purpose 10 c.c. of the standard arsenious solution are mixed with a few drops of starch-solution, and the iodine-solution added from a burette till the appearance of a blue colour. Suppose 10·2 c.c. iodine-solution are required for this: 1 c.c. iodine-solution corresponds to $\frac{10}{10·2} = 0·98039$ c.c. arsenious solution.

There are further required:

3. A clear, dilute, freshly prepared starch-solution.

4. Iodine-starch-paper, prepared by dipping strips of paper (free from chlorine) in a solution of iodide of potassium mixed with starch, and drying them. They must not be turned blue by pure hydrochloric acid.

This process can be applied to the estimation of a great variety of substances. The following are some of the most important.

a. *Arsenious anhydride.* — From 0·1 to 0·2 grm. of the sample are dissolved in a solution of acid carbonate of sodium, a few drops of starch-solution added, and then the iodine-solution till the appearance of the blue colour.

Example.—1 c.c. iodine-solution = 0·98039 c.c. arsenious solution. Weight of substance, 0·1 grm. Iodine-solution employed, 15·5 c.c. corresponding to 15·196 c.c. arsenious solution = 0·0752 grm. arsenious anhydride = 75·2 p. c.

b. *Iodine.* — The weighed sample is dissolved in a known volume of the arsenious solution, starch-solution added (if a blue colour is produced, more arsenious solution must be added), and the excess of arsenious anhydride estimated by the iodine-solution. — 1 c.c. arsenious solution = 0·0127 grm. iodine.

c. *Chlorine.* — (Chloride of lime, chlorine-water, &c.) — About 1 grm. chloride of lime is stirred up with water, and the arsenious solution added from a burette, until a drop of the mixture does not colour the iodine-starch-paper blue. Starch-solution is then added, and the excess of arsenious anhydride estimated by the iodine-solution. The amount of arsenious acid oxidised by the available chlorine in the sample, and hence that of the chlorine itself, is thus determined. For chlorine-water, a known volume of it is introduced from a pipette into a solution of carbonate of sodium, and the mixture treated as above.—1 c.c. arsenious solution = 0·00355 grm. chlorine.

Example.— 1 c.c. iodine-solution = 1 c.c. arsenious solution. Weight of chloride of lime, 1 grm. Arsenious solution employed, 72 c.c. Iodine-solution employed, 0·2 c.c. Amount of arsenious anhydride oxidised, 71·8 c.c. Available chlorine, 71·8 × 0 00355 = 0·25489 = 25·489 p. c.

d. *Hydrosulphuric acid.*—A known volume of the standard arsenious solution is introduced into a graduated cylinder, and a known volume of sulphuretted-hydrogen-water added, the arsenious solution being in excess. The mixture is briskly agitated, acidulated with hydrochloric acid diluted to about ten times its volume, and filtered into a dry vessel from the precipitated tersulphide of arsenic. An aliquot part of the filtrate is measured off, neutralised with powdered acid carbonate of sodium, starch-solution added, and the excess of arsenious anhydride determined by the iodine-solution. The amount found, calculated for the whole of the filtrate, and deducted from the weight of arsenious anhydride employed, gives the amount precipitated by the hydrosulphuric acid. 1 atom arsenious anhydride reacts with 3 atoms hydrosulphuric acid ($As^2O^3+3H^2S=As^2S^3+3H^2O$): hence, 1 c.c. arsenious solution, containing 0·00495 grm. anhydride, corresponds to 0·00255 grm. hydrosulphuric acid.

Example.—1 c.c. iodine-solution = 0·25974 arsenious solution.

$$\left.\begin{array}{l}\text{10 c.c. standard arsenious solution}\\ \text{20 c.c. sulphuretted hydrogen water}\end{array}\right\}\text{ diluted to 300 c.c.}$$

100 c.c. of the mixture required 11 c.c. iodine-solution: hence 300 c.c. require 33 c.c. iodine-solution, = 8·57 c.c. arsenious solution. 10 − 8·57 = 1·43 c.c. arsenious solution = 0·0036465 grm. hydrosulphuric acid. Whence 100 c.c. sulphuretted hydrogen water contain 0·01823 grm. hydrosulphuric acid.

e. *Chromates.*—All chromates, when boiled with hydrochloric acid, evolve for each atom of the salt 3 atoms chlorine ($Cr^2O^4H^2+6ClH=Cr^2Cl^3+4H^2O+Cl^3$): hence each atom of a bichromate evolves 6 atoms chlorine. If this chlorine be estimated by the process described in (c), the amount of chromate or bichromate is readily calculated from it. ($Cl^6 : Cr^4O^7K^2 :: 213 : 294{\cdot}8$).

From 0·2 to 0·4 grm. of the salt is placed, together with sufficient strong hydrochloric acid, in a small flask, to which is attached by a piece of caoutchouc tubing a glass delivery-tube, which passes loosely into the mouth of an inverted retort containing a known volume of the standard arsenious solution. The neck of the retort must be of sufficient capacity to contain the whole of the arsenious solution employed. Heat is then applied to the flask, when chlorine is evolved and passes into the solution in the retort. In order to avoid the possible absorption into the flask of the contents of the retort, the end of the delivery-tube which dips into the arsenious solution terminates in a piece of caoutchouc tubing which is closed with a piece of glass rod: in the caoutchouc tube a small slit is made, which serves as a valve, allowing the egress of the gas, but preventing the ingress of the liquid. When the whole of the chlorine has passed into the retort, the delivery-tube is withdrawn, the retort emptied into a beaker, starch added, and the unoxidised arsenious anhydride estimated by the iodine solution.

This method of analysis is applicable to all metallic peroxides which evolve chlorine when heated with hydrochloric acid.

The above method is a modification by Mohr of that introduced by Bunsen, who was the first to employ the reaction of iodine with reducing agents in volumetric analysis. The reducing agent employed by Bunsen was a very dilute solution of *sulphurous acid.* The use of this reagent is attended with some inconvenience, owing to the large quantity of it necessary for the operation, the difficulty of preserving it unchanged, and the introduction of another solution into the analysis, viz. a solution of iodide of potassium. Another reducing agent, which in many cases may replace without disadvantage Mohr's arsenious solution, is *hyposulphite of sodium*, which is converted by iodine into tetrathionate of sodium: the reaction takes place between 2 atoms of the salt and 2 of iodine ($2S^2O^3Na^2 + I^2 = S^4O^6Na^2 + 2NaI$). The formula of the crystallised salt is $S^2O^3Na^2 + 5H^2O = 248$: hence by dissolving 24·8 grm. (1 decigramme-atom) in 1 litre of water, a solution is obtained, of which each c.c. contains 0·0248 grm. hyposulphite, and corresponds to 0·0127 grm. iodine.

By means of this standard solution *copper* may be estimated volumetrically with great exactness. When iodide of potassium is added to the solution of a cupric salt, subiodide of copper is precipitated, and iodine set free ($Cu^2O + 2KI = Cu^2I + K^2O + I$), the atom of liberated iodine corresponding to 2 atoms copper; if therefore the amount of free iodine be estimated by the standard solution of hyposulphite, that of the copper is easily calculated from it. The copper is dissolved in dilute nitric acid, and the solution boiled till free from nitrous acid; it is then moderately diluted, neutralised with carbonate of sodium, and acidulated with acetic acid. A quantity of iodide of potassium in crystals, not less than 6 times the weight of the copper, is then added; and when it has dissolved, the standard solution of hyposulphite is added, till the colour of the solution changes from brown to yellow. After the addition of a little clear starch-solution, the hyposulphite is further added till the blue colour has entirely disappeared. 1 c.c. hyposulphite = 0·00634 grm. copper. Small quantities of iron, tin, lead, or zinc, do not interfere with this estimation. (Brown. Chem. Soc. Qu. J. x. 71.)

41. Estimation of Iodine in metallic Iodides.

a. *In absence of Bromides.*—Bisulphide of carbon, or chloroform, is coloured violet by free iodine, or by chloride or terchloride of iodine, but is not affected by pentachloride, ICl^5. Upon this fact is founded a method for the estimation of metallic iodides, by determining the amount of chlorine required to convert into pentachloride the iodine contained in the iodide.

Standard solution: a very dilute aqueous solution of chlorine, of known strength. Chlorine-water is added to a large quantity of water, and the amount of chlorine in a measured volume of the mixture determined by one of the chlorimetrical processes: and from this the amount of chlorine in one division of the burette is calculated = x.

The solution to be analysed (which must not contain any metallic salts that are decomposed by chlorine or iodine) is largely diluted, and mixed in a stoppered vessel with a few grammes of pure bisulphide of carbon (or chloroform), and the dilute standard solution of chlorine gradually added, the mixture being briskly agitated, until the violet colour that at first appears is entirely gone. Let the number of burette-divisions employed = T: then Tx is the amount of chlorine, from which the amount of iodine in the sample is to be calculated. The reaction takes place between six atoms chlorine and one atom iodine. ($Cl^6 : I :: 213 : 127$.)

If organic matter be present in the solution examined, an excess of chlorine over the normal amount is required for the destruction of the violet colour. In this case, when the colour has disappeared, an excess of pure iodide of potassium is added, and the amount of iodine set free determined as in 40. Every six atoms of liberated iodine corresponds to one atom of iodine in the original solution ($ICl^5 + 5KI = I^6 + 5KCl$).

6. *In presence of Bromides.*—When a solution contains a bromide as well as an iodide, it must be diluted till there is not more than 1 pt. of the former to 13,000 pts. water. Pentabromide of iodine which, on addition of chlorine to this dilute solution, is formed either alone or together with pentachloride, according to

the amount of bromide present, resembles the pentachloride in its behaviour to bisulphide of carbon or chloroform. Since the amount of chlorine employed is just the same as if no bromide were present, the requisite calculation is the same as in (a).

42. **Estimation of Silver** (in alloys or solutions).

This estimation depends upon the property possessed by chloride of silver of aggregating into masses, and rapidly subsiding in a solution. 1 atom silver=108, dissolved in nitric acid, requires 1 atom chloride of sodium=58·5 for its complete precipitation. Hence if a silver-solution be completely and accurately precipitated by a chloride of sodium solution of known strength, the amount of silver is readily calculated. The standard solutions required are:

a. *A normal solution of chloride of sodium.*—5·417 grm. pure decrepitated chloride of sodium are dissolved in distilled water (perfectly free from chlorine) and diluted to 1000 c.c.: (or 16·98 c.c. of a solution of chloride of sodium saturated at the ordinary temperature are diluted to 1000 c.c.): 1 c.c.=0·010 grm. silver.

b. *A decimal solution of chloride of sodium.*—100 c.c. of solution a, are diluted with distilled water to 1000 c.c. 1 c.c.=0·001 grm. silver.

c. *A decimal silver-solution.*—1 grm. chemically pure silver is dissolved in nitric acid perfectly free from chlorine, and the solution diluted to 1000 c.c. 1 c.c. contains 0·001 grm. silver.

Equal volumes of b. and c. mixed together, should yield a solution containing neither chlorine nor silver.

About 1 grm. of the substance to be analysed is dissolved in nitric acid with the aid of heat, the excess of acid evaporated off, the solution diluted, and filtered into a stoppered vessel. The normal chloride of sodium solution is then added from a burette, the mixture being briskly shaken from time to time, as long as it produces a distinct precipitate. As soon as the liquid is quite clear, 1 c.c. of the decimal chloride of sodium solution is added; if the liquid remains clear, the chloride of sodium is already in excess; if a precipitate is formed, the decimal solution must be added drop by drop, with occasional agitation, until it no longer produces any effect. The excess of chloride of sodium is then estimated in precisely the same manner by the decimal silver-solution. If the amount of silver in the alloy be already approximately known (by cupellation or otherwise) the simplest way is to weigh out as much of the alloy as contains about 1 grm. silver, to add at once 100 c.c. of the normal chloride of sodium solution, and to complete the estimation with the decimal solutions, as above.

43. Estimation of soluble Chlorides by Nitrate of Silver.

This estimation depends on the fact that nitrate of silver, when added to a *neutral* solution containing a chloride and a chromate, does not precipitate red chromate of silver, until the whole of the chlorine is precipitated. The solutions required are:

a. *A standard decimal solution of nitrate of silver.*—10·8 grm. pure silver are dissolved in nitric acid, evaporated to dryness, the residue carefully fused, and dissolved in water, and the solution diluted to 1000 c.c. : or 17 grm. fused nitrate of silver are dissolved and diluted to 1000 c.c. 1 c.c.=0·00355 grm. chlorine.

b. *A standard decimal solution of chloride of sodium.*—5·85 grm. decrepitated chloride of sodium are dissolved in water, and diluted to 1000 c.c. These two solutions, when mixed in equal volumes, must yield a solution containing neither chlorine nor silver.

c. *A solution of chromate of potassium*, which need not be standardised.

From 0·2 to 0·4 grm. of the substance to be examined are dissolved, and to the neutral or feebly alkaline solution a few drops of the chromate solution added; the silver-solution is then added until the permanent appearance of a red precipitate; and the point at which the red colour disappears is ascertained by means of the chloride of sodium solution. The volume of chloride of sodium solution is deducted from that of the silver-solution employed: and the amount of chlorine in the sample calculated from the remainder.

44. Estimation of Hydrocyanic Acid.

Two atoms cyanide of potassium with one atom nitrate of silver form one atom soluble cyanide of silver and potassium ($2CyK + NO^3Ag = Cy^2AgK + NO^3K$): which compound is decomposed by the further addition of nitrate of silver, a precipitate of cyanide of silver being formed ($Cy^2AgK + NO^3Ag = 2CyAg + NO^3K$). Hence, when a silver-solution is added to cyanide of potassium, the first appearance of a permanent precipitate marks the point at which the formation of the double salt is complete; and if the silver-solution be of known strength, the volume employed will indicate the amount of cyanogen present, 1 atom silver corresponding to 2 atoms cyanogen.

Standard solution.—6·3 grm. fused nitrate of silver are dissolved in water and diluted to 1000 c.c. 1 c.c.=0·002 grm. hydrocyanic acid. The solution containing hydrocyanic acid is mixed with caustic potash till it is decidedly alkaline, a few drops of chloride of sodium solution added, and then the standard solution until the precipitate formed does not disappear on agitation.

This is a convenient method of estimating hydrocyanic, in presence of hydrochloric, acid.

45. Estimation of Iron.

Permanganates are decomposed by protosalts of iron in presence of sufficient free acid, a protosalt of manganese being formed, while the protosalt of iron is converted into sesquisalt ($Mn^4O^8H^2 + 20FeCl + 14HCl = 4MnCl + 10Fe^2Cl^3 + 8H^2O$). So long therefore as an acid solution of iron contains any protosalt, it will destroy the colour of permanganate of potassium (cameleon). Cameleon is decomposed by concentrated hydrochloric acid in the cold, and by dilute hydrochloric acid when moderately heated, but cold dilute hydrochloric acid is without action upon it: hence the iron-solution should be very dilute, and should not be operated on when warm.

The only solution required is one of cameleon. This is prepared by moderately heating in a Hessian crucible a mixture of 8 pts. finely powdered binoxide of manganese, 10 pts. hydrate, and 7 pts. chlorate, of potassium, which have previously been stirred up with a little water, and evaporated to dryness. The fused mass is dissolved in hot water, mixed with a little sulphuric acid, and the clear solution poured off from the deposit (not filtered). As this solution cannot be kept unchanged, its standard must be determined before each experiment. For this purpose Mohr recommends the employment of crystallised sulphate of iron and ammonium ($SO^4FeNH^4 + 3H^2O$), which is obtained by crystallising a mixture of the sulphates of iron and of ammonium in atomic proportions. It can be kept for any length of time in the solid state, but not in solution. Exactly $\frac{1}{7}$th of its weight consists of iron. A weighed portion of the salt is dissolved in water, a little sulphuric acid added, and then the cameleon-solution from a burette until a rose-tint is produced, which does not disappear immediately. Suppose 1 grm. of the salt required 23·7 c.c. cameleon, these correspond to $\frac{1}{7}$ grm. = 0·14286 grm. iron, and 1 c.c. = 0·006 grm. iron. Or the cameleon may be standardised by the normal oxalic acid solution as in 39, 5 c.c. of which, containing 0·315 grm. oxalic acid = 0·28 grm. iron. The old method of standardising the cameleon by means of a solution of ferrous chloride obtained by dissolving clean iron wire in hydrochloric acid is less accurate, owing both to the impurity of the iron, and the extreme difficulty of obtaining a solution perfectly free from sesquichloride.

For the analysis of iron-ores, the substance, very finely powdered, is dissolved as completely as possible by digestion in strong hydrochloric acid: any sesquisalt that may be present is reduced by heating the solution with metallic zinc free from iron, until the red colour has entirely disappeared. It is then diluted to about 1 litre, and the cameleon-solution added until a rose-tint is produced that does not immediately disappear. The number of c.c. employed, multiplied by the amount of iron to which each c.c. corresponds, gives the amount of iron in the sample. When it is desired to estimate separately the ferrous and ferric salts in the sample, care must be taken to exclude the air during solution: this is done most simply by placing some acid carbonate of sodium in the flask in which the ore is dissolved. The amount of protosalt is then determined by the cameleon-solution, and, after reduction by zinc, the total amount of iron is estimated: the difference between the volumes of cameleon solution employed in each determination corresponds to the iron contained as sesquisalt.

46. **Valuation of Nitre.**

a. Six atoms of iron (168 pts.) in solution as protochloride require one atom of nitrate of potassium (101 pts.) for their complete conversion into sesquichloride. ($6FeCl + NO^3K + 4HCl = 3Fe^2Cl^3 + KCl + 2H^2O + NO$). If then a weighed sample of a substance containing nitre be made to act upon a measured excess of protochloride of iron, and the remaining protochloride be estimated by cameleon, the amount which has been converted into sesquichloride will indicate the quantity of nitre contained in the sample.

The standard solution of ferrous chloride cannot be kept, but must be prepared for each experiment. 2 grm. clean soft iron wire are dissolved in a flask by excess of concentrated hydrochloric acid: about 1·2 grm. of the sample of nitre are added, and the whole boiled till the dark colour produced by the absorption of nitric oxide by protochloride of iron has completely disappeared. In order to prevent as far as possible the access of air during the solution, the flask may be closed with a perforated cork, into which is inserted a tube drawn out to a fine point. Or the cork may be fitted with a bent tube, which passes nearly to the bottom of a second flask (loosely corked), containing water which has been freed from air by boiling: when the lamp is withdrawn from the first flask, the water will pass over into the iron-solution, which will thus be cooled without access of air. The solution is then diluted with (boiled) water to about 1 litre, and the remaining ferrous chloride estimated by the standard cameleon-solution (45). 2 grm. minus the amount of iron thus ascertained, gives the amount of iron converted by the nitre into sesquisalt; whence the amount of nitre in the sample is readily calculated. ($Fe^6 : NO^3K :: 168 : 101$.)* (Pelouze.)

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* In spite of the above precautions, it is almost impossible to prepare a solution of protochloride of iron perfectly free from sesquichloride: and thus a cer-

b. Gay-Lussac's method is to convert the nitrate of potassium into carbonate by ignition with carbon and decrepitated chloride of sodium: the carbonate is then estimated by alkalimetry (36), and the nitrate calculated from it. ($CO^3K^2 : 2NO^3K :: 138 : 202.$)

Abel and Bloxam (Chem. Soc. Qu. J. x. 108) recommend the following modifications of this method. The carbon employed should be graphite, prepared by Brodie's process: the best proportions are, 1 pt. nitre, 4 pts. chloride of sodium, and $\frac{1}{4}$ pt. graphite. The heat should not be sufficient to volatilise the chloride of sodium to any considerable extent: 8 to 10 minutes moderate redness in a muffle-furnace, or 20 minutes over a Bunsen's lamp will suffice. If the nitre contain any sulphate, the fused mass must be sprinkled with chlorate of potassium, and heated again as long as effervescence takes place.

c. For Pugh's process, *see* p. 9.

47. Estimation of Sugar and Starch.

1 atom of glucose ($C^{12}H^{24}O^{12}=360$), (also called grape-sugar, diabetic-sugar, or starch-sugar,) when in contact with an alkaline solution of cupric oxide at boiling heat, takes 5 atoms oxygen ($=80$) from 10 atoms oxide of copper, forming 5 atoms suboxide of copper ($10Cu^2O = 5Cu^4O = O^5$). The same amount of cupric oxide requires $1\frac{1}{3}$ atom milk-sugar ($C^{12}H^{20}O^{10}+2H^2O$) $=480$, for its complete reduction. If then, a standard alkaline solution of cupric oxide be mixed at boiling heat with a solution containing grape- or milk-sugar until its reduction is complete, the amount of sugar may be calculated from that of reduced suboxide.

The standard solution is prepared by dissolving 34·64 grm. sulphate of copper (purified by recrystallisation from water containing sulphuric acid, after previous treatment with nitric acid)

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tain amount of error is inseparable from this method. For this reason it is advisable before operating on an unknown substance, to make a determination with a known weight of pure nitre, the results of which may serve as a term of comparison for the other analysis (Mohr). Fresenius (Ann. Ch. Pharm. cvi. 217) obtains good results by preparing the iron-solution and decomposing the nitrate in a vessel filled with hydrogen. According to Abel and Bloxam (Chem. Soc. Qu. J. ix. 110) the method is not free from other sources of error.

in 200 c.c. water, mixing it with a solution of 173 grm. tartrate of potassium and sodium in 480 c.c. caustic soda of sp. gr. 1·14, and diluting the mixture to 1000 c.c. at 15°. 10 c.c. of this solution (which has a fine blue colour) corresponds to 0·05 grm. dry grape-sugar, and to 0·067 grm. milk-sugar, dried at 100°.

A known weight of the liquid whose sugar is to be estimated, is diluted to 10—20 times its volume, so that it does not contain more than 1 p. c. sugar. If it contains any albuminous substances, they are removed by basic acetate of lead. 10 c.c. of the standard copper-solution are diluted with 40 c.c. water, the whole boiled, and while boiling, the sugar-solution is added from a burette, until the reduction of the copper is complete — *i. e.* until the solution is colourless. To perceive this, the red precipitate must be allowed to subside. So long as each fresh drop of sugar-solution produces a yellow cloud on the surface of the liquid, the reduction is not complete; the nearer it approaches completion, the redder and more abundant does the precipitate of cuprous oxide become. A few drops of the liquid are then filtered and tested for copper with hydrosulphuric acid*, or, after acidulation with acetic acid, by very dilute ferrocyanide of potassium; if copper be found, more sugar-solution must be added. Suppose 10 c.c. sugar-solution have been employed. In order to control the result, the experiment is repeated with the same quantities of copper- and sugar-solution, the precipitate is allowed to settle, and the solution filtered as quickly as possible. If it be found free from copper, the experiment is repeated with a somewhat less volume of sugar-solution, say 9·6 c.c. If copper be then found in the filtrate, the sugar-solution contains between 5 and 5·2 grm. dry grape-sugar, or the corresponding amount of milk-sugar, in 1000 c.c.

In order to estimate cane-sugar or starch by this process, they must be converted into glucose by digestion at a gentle heat for some hours with dilute sulphuric, or tartaric, acid: 100 pts. grape-sugar ($C^{12}H^{24}O^{12}$) correspond to 95 pts. cane-sugar ($C^{12}H^{22}O^{11}$), or to 90 pts. starch, $C^{12}H^{20}O^{10}$. Milk-sugar is also converted into glucose by heating with dilute sulphuric acid. According to Fehling (Ann. Ch. Pharm. cvi. 79) milk-sugar cannot be accurately estimated unless it is first converted into glucose.

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* If the solution has been treated with acetate of lead, it cannot be tested by hydrosulphuric acid.

48. **Analysis of Milk.**

A known weight of milk (15—20 grm.) is evaporated to dryness in a water-bath with a weighed amount (3—4 grm.) of sulphate of calcium, which has been ignited, moistened, and again dried. By weighing the residue the total amount of the non-volatile constituents is ascertained, as well as (by loss) that of the water. A weighed portion of the residue is then repeatedly treated with ether, the insoluble portion dried, and weighed: the loss of weight represents the butter. The portion insoluble in ether is then repeatedly treated with boiling alcohol, again dried, and weighed: the loss of weight represents the milk-sugar and the salts which are soluble in alcohol. The weight of the residue minus that of the sulphate of calcium added, represents the casein and insoluble salts. For the determination of the non-volatile salts, another portion of the milk is evaporated to dryness, the residue ignited till all the carbon is burnt off, and then examined as directed in 30. For the direct estimation of the milk-sugar, about 50—60 grm. milk are mixed with acetic acid, heated to 50° or 60°, filtered, and the whey thus obtained treated with the standard copper-solution, as in 47.

49. **Estimation of the hardness of Water.**

The *hardness* of water depends upon the amount of calcium- or magnesium-salts which it contains. A dilute aqueous solution of soap when agitated forms a froth upon its surface. Salts of calcium or magnesium are decomposed by alkaline soaps, with formation of an insoluble lime- or magnesia-soap. Hence water containing calcium- or magnesium-salts, when agitated with a soap-solution, does not give a permanent froth until all the calcium or magnesium is precipitated, and the soap-solution is present in excess. If therefore it has been determined by previous experiment what volumes of a standard soap-solution are required to precipitate completely, and give a permanent froth with, different calcium-solutions of known strengths, this soap-solution may be employed to determine an unknown amount of lime in any water. The standard solutions required are:

1. *An alcoholic solution of soda-soap.*—30 grm. well dried soda-soap, containing about 12 p. c. water, are dissolved in 3 litres alcohol of 86 p. c., and the solution filtered. 200 grm. of this solution are then mixed with 150 grm. water, and with 180 grm. alcohol of 48 p. c. A solution is thus prepared, 45 c.c. of which will completely precipitate the calcium in, and give a permanent foam with, 100 grm. water containing ·012 grm. lime.

2. *A perfectly neutral standard solution of chloride of calcium.*—0·2143 grm. pure carbonate of calcium are dissolved in hydrochloric acid, evaporated to dryness, the residue dissolved in water and diluted to 1000 c.c. 100 c.c. of this solution contain as much chloride of calcium as corresponds to ·012 grm. lime (Ca^2O).

3. By means of this calcium-solution, 23 weaker solutions are prepared, the first and weakest of which contains ·0005 grm. lime in 100 grm., each successive one being stronger than that immediately preceding by ·0005 grm.: the original solution (2) containing ·012 grm. is the 24th in the series.

100 grm. pure water are then placed in a stoppered bottle holding 300—400 c.c., and the bottle is labelled No. 1: and 100 grm. of the 24 calcium-solutions are placed in similar bottles, which are labelled Nos. 2—25 respectively. The next step is to ascertain, beginning with No. 1, how much of the standard soap-solution (which is added from a burette graduated to $\frac{1}{10}$ c.) is required to produce a thick, soft, and permanent lather when agitated with the contents of each flask successively. A table is thus constructed showing how much of the soap-solution corresponds to ·0005, ·0010, ·0015, ·0020, and so on up to ·0120 grm. lime in 100 grm. water. The number of milligrammes of lime contained in 100 grm. of any water is spoken of as its *degree of hardness.*

The above method is not applicable to the estimation of the hardness of any water which contains more than ·012 grm. lime in 100 grm.: in waters containing more lime than this, a permanent (though tough and flaky) lather is produced before the precipitation of the whole of the calcium. The water is therefore diluted, if necessary, and then treated with the soap-solution as above. The number of c.c. of soap-solution employed, compared with the numbers in the table, give the amount of lime contained in the water. Magnesium-salts behave with soap-solution just like lime-salts: if therefore the water contains magnesia, it will be represented in the result obtained by an equivalent amount of lime. When a water contains, besides other calcium-salts, carbonate of calcium dissolved in free carbonic acid, it is rendered less hard by boiling. The *gross hardness* is in this case determined in a portion of the fresh water: the *permanent hardness*, in an equal portion after boiling: the difference between the two amounts obtained represents the *temporary hardness*.

50. **Analysis of Urine.**

a. The specific gravity is first taken (31).

b. The total amounts of *water*, *organic matter* and *non-volatile salts*, are ascertained by evaporating to dryness a known weight (15 — 20 grm.) of urine, and weighing the residue after heating to 110° : the loss of weight represents the water. The residue is then ignited in a porcelain crucible, with occasional addition of nitric acid, till all the carbon is burnt off, and again weighed: the loss of weight represents the organic matter and volatile salts. The second residue consists of the non-volatile salts: it is analysed as directed in 30.

c. *Uric Acid.*—A larger quantity of urine (200 grm.) is acidulated with hydrochloric acid, and allowed to stand for two days: the uric acid separates out, and is collected on a weighed filter. Or the urine may be evaporated to dryness, and that portion of the residue which is insoluble in alcohol treated with dilute hydrochloric acid, which leaves the uric acid undissolved.

d. *Chloride of Sodium.*—Neutral or feebly acid solutions of urea give with a dilute solution of nitrate of mercury a white precipitate, which contains 2 atoms mercuric oxide to 1 atom urea: chloride of mercury does not form this precipitate with urea: chloride of sodium and nitrate of mercury mutually decompose each other, forming nitrate of sodium and chloride of mercury:

the decomposition takes place between 1 atom of each salt ($NO^3Hg + ClNa = NO^3Na + ClHg$). Hence when nitrate of mercury is added to a solution containing both urea and chloride of sodium (*e.g.* urine), a permanent precipitate is first produced when all the chloride of sodium has been converted into nitrate: and if a standard solution of nitrate of mercury be used, the amount of chloride of sodium present is readily calculated from the volume of mercury-solution employed.

The solutions required are:

1 *A standard solution of chloride of sodium* (A).—Pure water at the ordinary temperature dissolves an invariable amount of pure rock-salt. 20 c.c. of the saturated solution, containing 6·368 grm. salt, are diluted to 318·4 c.c.: 1 c.c. of this solution contains ·02 grm. chloride of sodium.

2. *A standard solution of urea*, containing 4 grm. urea in 100 c.c. 1 c.c. contains ·04 grm. urea.

3. *A standard solution of nitrate of mercury.*— Crystallised subnitrate of mercury is dissolved in nitric acid, and heated till a drop of the solution is not precipitated by chloride of sodium: it is then evaporated to a syrup and diluted with ten times its volume of water. In order to standardise this solution, 10 c.c. of the chloride of sodium solution are mixed with 3 c.c. of the urea-solution, and 5 c.c. of a cold saturated solution of sulphate of sodium* perfectly free from chlorine. The mercury-solution is then added from a burette, the mixture being continually agitated, until a permanent precipitate is produced. If the mercury-solution be too concentrated, it cannot be graduated correctly. Suppose for instance, 7·8 c.c. are required to produce the precipitate, the solution is too concentrated: it must be diluted with its own volume of water, and the experiment repeated. If 15·5 c.c. be now required, 155 vols. of the solution are diluted to 200 vols.: when a solution is obtained, 1 c.c. of which corresponds to ·01 grm. chloride of sodium. (If any foreign metals are present in the mercury-solution, an opalescence may be produced when it is first added to the solution of chloride of sodium and urea: but as this

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* In order to remove the free nitric acid which is always contained in the mercury solution ($NO^3H + SO^4Na^2 = NO^3Na + SO^4NaH$).

is not sensibly increased by further addition of the mercury-solution it is easily distinguished from the urea-precipitate).

Before the chloride of sodium in urine can be determined by means of this solution, the phosphates and sulphates present in the urine must be removed: this is done by a mixture of 2 vols. of a cold saturated solution of baryta-water, and 1 vol. of a cold saturated solution of nitrate of barium (which must be free from chlorides or hyposulphites). 2 vols. urine are mixed with 1 vol. mixture, the precipitate filtered off and the alkaline filtrate neutralised with nitric acid. 15 c.c. of the filtrate (=10 c.c. urine) are taken for the determination; and the mercury-solution is added until a permanent precipitate is produced. Suppose 12·5 c.c. mercury-solution are required; the amount of chloride of sodium is 0·125 grm.

In very accurate analyses the chlorine must be removed from urine before proceeding to determine the urea by the mercury-solution. This is done by nitrate of silver. If 2·906 grm. fused nitrate of silver are dissolved in water, and diluted to 100 c.c., a solution is obtained 1 c.c. of which corresponds to ·01 chloride of sodium, and therefore to 1 c.c. of the mercury-solution. When, therefore, the volume of mercury-solution corresponding to the chloride of sodium in 10 c.c. urine has been determined above, the addition of the same vol. of silver-solution to another 10 c.c. of the same urine exactly removes the chlorine, and the estimation of the urea can be proceeded with at once.*

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* Phosphate of sodium, like urea, gives a precipitate with nitrate, not with chloride, of mercury. Hence this salt may be employed instead of urea to determine the amount of nitrate in a solution of nitrate of mercury. Chloride of sodium, as we have seen, decomposes nitrate of mercury, atom for atom, forming nitrate of sodium and chloride of mercury. If, therefore, 1 atom chloride of sodium be added to a solution of phosphate of sodium, 1 atom of nitrate of mercury is required for its decomposition, and a permanent precipitate does not appear till more than 1 atom of the latter is added. Similarly, when a solution of phosphate of sodium is precipitated by nitrate of mercury, it requires 1 atom of chloride of sodium for each atom of nitrate, to redissolve the precipitate. Hence, by means of a chloride of sodium solution of known strength, the amount of nitrate in a solution of unknown strength may be determined by the proportion $NaCl : NO^3Hg :: 58·5 : 162$. The solutions required are:

1. *A cold saturated solution of phosphate of sodium free from chlorine.*

c. *Urea.*—This estimation depends upon the fact that urea is precipitated by nitrate of mercury, when the nitric acid that is formed by the decomposition of the nitrate is neutralised by baryta-water or carbonate of sodium. The precipitation is complete as soon as the supernatant fluid contains mercury, which is ascertained by its giving a distinct yellow colour with carbonate of sodium. The reaction takes place between 1 atom urea (=60) and 4 atoms nitrate of mercury (=648): hence, theoretically, 0·1 grm. urea requires 1·080 grm. nitrate of mercury for its complete precipitation. It is found, however, in practice that, for 0·1 grm. urea 1·158 grm. nitrate is required in order to produce the yellow colour with carbonate of sodium in dilute solutions. The standard solutions required are: —

1. *A solution of urea*, containing 4 grm. urea in 200 c.c.: 1 c.c. contains ·02 grm. urea.

2. *A solution of nitrate of mercury*, 10 c.c. of which contain 1·158 grm. nitrate, and correspond to 0·1 grm. urea. This is prepared by dissolving 100 grm. pure mercury in nitric acid, heating till nitrous fumes are no longer evolved, evaporating to a syrup, and diluting with water to 1400 c.c. If the solution be prepared from crystallised subnitrate of mercury, it must be standardised as directed at p. 265 by means of the chloride of sodium solution (B.),

2. *A standard solution of chloride of sodium* (B).—20 c.c. of a cold saturated solution of rock-salt are diluted to 586·8 c.c. 1 c.c. (= ·010852 grm. chlor. sod.) corresponds to ·03 grm. nitrate of mercury.

If the mercury-solution be too concentrated, it cannot be estimated accurately; it should not contain more than 0·3 grm. nitrate in 10 c.c. In order to determine the concentration, 10 c.c. chloride of sodium solution are mixed with 4 c.c. phosphate of sodium solution, and the mercury-solution added from a burette until a permanent precipitate is formed. Supposing 5 c.c. to be required, the mercury-solution must be diluted with its own volume of water. 10 c.c. of the dilute mercury-solution are then mixed with 4 c.c. phosphate, and the chloride of sodium solution added *immediately* from a burette with continual agitation, until the precipitate is just dissolved. Suppose 12·5 c.c. are required. In order to control the determination 12·5 c.c. chloride of sodium solution are mixed with 4 c.c. phosphate, and the mercury-solution added till a permanent precipitate is formed. Suppose 10·25 c.c. are required: then by the first experiment 12·5 c.c. chloride of sodium solution correspond to 10 c.c., by the second to 10·25 c.c. mercury-solution: hence 10·12 c.c. mercury-solution (the mean between these two numbers) contain 12·5 × ·03 = ·375 grm. nitrate of mercury.

so that 10 c.c. mercury-solution correspond to rather more than 38·5 c.c. chloride of sodium solution. The mercury-solution, prepared by either of these methods, closely approximates to the required standard: it must be accurately standardised by means of the urea-solution. To 10 c.c. of the latter (=0·2 grm. urea) the mercury-solution is added from a burette until a drop of the mixture placed on a watch-glass gives a distinct yellow colour when mixed with a drop of carbonate of sodium. Supposing 19·25 c.c. mercury solution to be required for this, every 192·5 vols. must be diluted to 200 vols., and the experiment repeated: if the yellow colour be now produced with exactly 20 c.c. the solution is accurately standardised.

For the determination of urea in urine, 2 vols. urine are mixed as before with 1 vol. barium-solution, filtered, and to 15 c.c. of the filtrate (without previous neutralisation) the mercury-solution added from a burette until a drop of the supernatant fluid gives a distinct yellow colour with carbonate of sodium. The presence of chloride of sodium interferes with the accuracy of the determination, making the urea come out too high: hence, in very accurate analyses the urine must be previously freed from chlorine by the standard silver-solution, as above directed. In ordinary cases, however, this is not necessary: for sufficiently accurate results are obtained by deducting 2 c.c. from the volume of mercury-solution employed.

It is found by experiments with pure urea-solutions that, in the analysis of urines rich in urea, the yellow colour which marks the end of the reaction is produced by a somewhat smaller volume of mercury-solution than is actually necessary to precipitate the urea, so that the result obtained is somewhat too low: and, on the other hand, when the urine is poor in urea, a somewhat larger volume of mercury solution is required, so that the result is somewhat too high. In order to obviate the former source of error, the determination is repeated with another 15 c.c. of the filtered urine, to which 1 c.c. water is added for each 2 c.c. over 30 c.c. of mercury-solution employed in the first determination. In the latter case it suffices to deduct 0·1 c.c. for every 5 c.c. below 30 c.c. of mercury solution employed: *e. g.* if 25 c.c. mercury-solution were employed, the real amount is taken at 24·9 c.c. =0·249 grm. urea.

A very simple method for the determination of urea is founded on the fact that urea is completely decomposed by a solution of a hypochlorite, all its nitrogen being evolved in the gaseous form: (probably according to the equation $CH^4N^2O+3ClONa=CO^2+2H^2O+3ClNa+N^2$). If therefore the volume of nitrogen evolved from a given volume of urine be observed, the amount of urea is easily calculated. 1000 c.c. nitrogen at 0° and 760 mm. weigh 1·2609 grm.; 1 c.c. weighs ·0012609 grm. The weight of nitrogen evolved being thus determined, the corresponding weight of urea is given by the proportion 14 : 60 : : wt. of nitrogen : wt. of urea. The determination is thus performed. A graduated tube of stout glass, closed at one end, is about one-third filled with mercury, a known volume of urine introduced, and the tube filled with a solution of hypochlorite of sodium. The mouth of the tube is then closed tightly with the thumb, and the tube inverted into a vessel of mercury, or into a saturated solution of common salt. The decomposition, which commences almost immediately, is usually complete in 3 or 4 hours: during which time no attention is required. When the evolution of gas has quite ceased, the volume of nitrogen enclosed in the upper part of the tube is read off, and the calculation made. In very accurate experiments correction for temperature and pressure must be made: but ordinarily this is not necessary. In order to ensure the hypochlorite being in excess, not less than 5 or 6 times the volume of urine should be employed. The results are not materially affected by the ammonia and uric acid ordinarily present in urine: if, however, an undue amount of these substances be present, they should be previously removed by heating the urine with baryta-water as long as the smell of ammonia is perceptible. (Davy. Phil. Mag. [4.], vii. 385.)

f. *Ammonia.*—20 c.c. urine are introduced into a porcelain basin, over which is placed, supported by a glass triangle, another basin containing 10 c.c. of the standard acid solution (36). About 10 c.c. milk of lime are then added to the urine, and the whole placed on a ground glass-plate, covered with a bell-jar, and allowed to stand for 48 hours. All the ammonia in the urine is absorbed by the acid, the excess of which is finally determined as in 37.

g. *Phosphoric Acid.*—The only volumetric method for determining the phosphoric acid in urine is very complicated and tedious, and does not give very accurate results. It is far simpler to estimate the phosphoric acid by weight. The addition of excess of baryta-water to urine precipitates all the phosphoric and sulphuric acids as phosphate and sulphate of barium. From this precipitate the phosphate is dissolved by dilute hydrochloric acid, the barium precipitated from the solution by sulphuric acid, and the phosphoric acid from the filtrate by sulphate of magnesium, ammonia, and chloride of ammonium (6. a).

h. *Other Constituents.*—*Sugar* is estimated as directed in 47. *Albumen* is precipitated by heating the urine, after the addition of a few drops of nitric acid. For the detection of *lactic acid*, *see* p. 74.

PART V.

EXAMINATION FOR POISONS IN JUDICIAL INVESTIGATIONS.

1. **Examination for Arsenic.**

The object of the chemist, when employed in the detection of arsenic in cases of poisoning, is to separate the arsenic in the metallic state, and to produce it as such before the Court; since it is only in that form that the poison possesses properties so decidedly characteristic that it cannot possibly be confounded with any other substance.

The form in which arsenic can be most easily procured, and in which consequently it is most frequently met with in cases of poisoning, is that of *arsenious anhydride*, commonly called *white arsenic*. It occasionally happens that this substance may be found undissolved in the stomach, intestines, or vomited matter, and may be separated by mechanical means; it is always advisable, therefore, before proceeding to a chemical investigation, to ascertain by careful examination whether any of the poison can be detected unchanged in the substances submitted for analysis. For this purpose the substances to be examined are spread out in new and clean porcelain dishes, and turned over with clean glass-rods; or they may be mixed with water, and the lighter organic matter separated from the heavier arsenious anhydride by levigation. If any white grains are thus found which possess the characteristic properties of arsenious anhydride (p. 80), it is only necessary to reduce them to the metallic state by means of charcoal (p. 83), or in a Marsh's apparatus (p. 82).

It more frequently happens, however, that the poison cannot be detected or separated by mechanical means, but exists in a state of solution in, or of intimate mixture with, the contents of the stomach, &c. In this case the problem consists in dissolving and destroying by appropriate reagents the whole of the organic matter composing the contents, the vomited matter, the food, and even the stomach and intestines themselves. Until this is done, the detection of the arsenic is impossible.

It is of course indispensable, before proceeding to this operation, to ascertain by most careful examination that no arsenic is contained in any of the reagents (sulphuric, hydrochloric, and nitric acids, zinc, nitre, chlorate of potassium, potash, &c.), or in any of the vessels employed. This is equally essential, whether the reagents have been purchased, or prepared by the operator himself. It is most readily done by testing them in a Marsh's apparatus; for this purpose the chlorate of potassium is converted by fusion into chloride, the nitre and potash into sulphate by sulphuric acid. And if, when all these precautions have been duly observed, arsenic be found in the body, it must not be forgotten that it may have been introduced accidentally by the administration of certain medicines, such as preparations of antimony or phosphorus: even sesquihydrate of iron, which is frequently administered as an antidote, may contain arsenic, unless prepared with great care.

There are several methods of extracting the arsenic in a form available for chemical analysis, most of which involve the destruction of the organic matter in which it is contained. 1. When the substance is in the form of a paste (as in the contents of the stomach and the fæces), it is gently heated and completely saturated with washed chlorine, which is evolved from binoxide of manganese and hydrochloric acid, both of which have been previously tested for arsenic. When the mass is completely saturated and bleached, it is heated nearly to boiling, to expel the excess of chlorine, and the solution, which contains all the arsenic, filtered through paper free from smalt. 2. The stomach and intestines, with their contents, are cut into shreds, and dissolved in a porcelain dish by as little caustic potash as possible: the solution is acidulated with dilute sulphuric acid, and the coagulated mass treated with chlorine, as above. 3. The organic matter is cut into pieces, and treated with sufficient water to form a thin paste, and a quantity of concentrated hydrochloric acid, equal in weight to the organic matter, is added. The whole is then heated in a water-bath, stirred every few minutes, and chlorate of potassium (free from lead) gradually added, until a clear yellow solution is obtained. This is heated for some time longer, filtered when cold through linen, or paper free from smalt, the residue on the filter washed with hot water as long as the washings have an acid reaction, and the filtrate evaporated on a water-bath to about 1 lb.

4. The whole of the substances to be examined, both solid and liquid, is introduced into a large tubulated retort, with about an equal weight of fused chloride of sodium, or rock-salt in fragments: the retort is connected with a receiver furnished with a delivery-tube, which dips into water. A quantity of sulphuric acid not sufficient to decompose all the chloride of sodium is poured into the retort; and when the evolution of hydrochloric acid has ceased, the contents of the retort are heated to boiling, and the chloride of arsenic which distils over is collected in the receiver, which is kept quite cool. Since the greater part of the arsenic comes over towards the end of the operation, the distillation should be carried as far as possible.

The solution obtained by any of these methods is poured into a flask, and completely saturated with washed hydrosulphuric acid, while it is heated to about 60° or 70°, to facilitate the precipitation of the sulphide of arsenic. After standing for 24 hours, the solution is poured off as far as possible from the precipitate, which is thrown upon the smallest possible filter, and washed with water containing hydrosulphuric acid. The filtrate, before being thrown away, should be again saturated with hydrosulphuric acid. The precipitate, which, even if much arsenic be present, is generally of a dirty-greyish colour *, contains organic matter, which must be removed. For this purpose the precipitate is dissolved in dilute ammonia, or in a concentrated solution of carbonate of

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* The precipitate may also contain, as sulphides, any of the metals which are precipitated by hydrosulphuric acid from an acid solution (antimony, lead, mercury, copper), by which the yellow colour of sulphide of arsenic would be disguised. They are left undissolved when the precipitate is treated with ammonia. Zinc, if present, will be found in the original filtrate.

ammonium, the solution evaporated to dryness, and the residue warmed with concentrated nitric acid (free from chlorine) in a porcelain crucible, till it is all dissolved: the solution is neutralised with caustic soda or carbonate of sodium, evaporated to dryness, and the residue heated to fusion. More nitrate of sodium may be added if necessary: when sufficient is present, the heated residue becomes first brown, then black, and finally fuses without detonation to a colourless liquid. The fused mass, when cool, is gently heated with concentrated sulphuric acid till the nitric acid is completely expelled, dissolved in as little hot water as possible, and the solution introduced slowly and gradually into a Marsh's apparatus through the funnel-tube. The hydrogen in the apparatus is evolved from zinc and sulphuric acid, both previously tested for arsenic: the latter is added gradually, to avoid too great evolution of heat. Before introducing the arsenic-solution the apparatus should be full of hydrogen, and the long difficultly-fusible delivery-tube should be heated to redness in one spot. If, after heating the tube for an hour, no metallic mirror is obtained, nor any metallic stains upon a fragment of porcelain depressed into the flame of the kindled gas, the absence of arsenic may be regarded as certain. If a mirror and metallic stains be obtained, they must be proved to possess the physical and chemical properties of arsenic described at pp. 82, 83. If sufficient arsenic be present, it is advisable to obtain mirrors in different parts of the delivery-tube: the most characteristic of them having been selected, the portion of the tube containing it is cut off, sealed at both ends, and preserved for production before the court. When the amount of arsenic is very small, it is difficult to obtain satisfactory proof of the nature of the deposit: the only indication which is perfectly conclusive is the production of a metallic mirror which volatilises when gently heated, and is again deposited in the cool part of the tube, at the same time imparting to the evolved gas the characteristic smell of garlic.

If no arsenic be found in the stomach and intestines, it may have been partly carried away in the fæces and vomited matter, partly absorbed into the blood, and into those organs which are rich in blood. It is then necessary to examine the liver, spleen, lungs, heart, and kidneys, by some of the methods above described. If any urine be found in the bladder, it should be examined first, by acidulation with hydrochloric acid, and saturation with hydrosulphuric acid.

Wöhler gives the following method for the extraction of arsenic as especially applicable in cases when a body is exhumed entire after long interment. The whole of the soft parts are treated in a large porcelain dish with moderately strong nitric acid, and heated on a sand-bath with constant stirring, until they are converted into a homogeneous paste. The paste is neutralised by caustic potash or carbonate of potassium, and a quantity of nitre added about equal in weight to the organic matter operated upon. The whole is evaporated to dryness, with constant stirring, and the residue introduced by degrees into a new Hessian crucible, heated to dull redness: in this manner the organic matter is completely destroyed, and the arsenic converted into alkaline arsenate. The amount of nitre added must be just enough to destroy all the organic matter, and no more: it is advisable to ignite a small portion of the mixture separately, and to observe whether it is quite white after ignition; if not, more nitre is required. The ignited mass is then dissolved in as little hot water as possible, and, without filtering, heated with sulphuric acid till all the nitric and nitrous acids are expelled. When cool it is stirred up with cold water, and the solution poured off from the residue, which is thoroughly washed. This solution contains all the arsenic as arsenate of potassium, and is treated with hydrosulphuric acid as above.

2. Examination for Phosphorus.

Only the ordinary phosphorus is poisonous: its action depends upon its oxidation into phosphorous acid.

The best method for the detection of phosphorus in cases of poisoning is to distil the suspected substance in a flask with water and sulphuric acid: the flask is fitted with a delivery-tube bent twice at right angles, the end of which dips into a receiver containing cold water, which must be kept cool. The distillation is performed in the dark. As soon as the vapours arrive in the cooled part of the tube, a continual phosphorescent light is observed therein, generally in the form of a shining ring: at the same time globules of phosphorus are deposited in the receiver. In this manner 1 part phosphorus may be detected in 100,000 parts substance. It is essential to produce in court the water which contains globules of phosphorus, or which exhibits a phosphorescent light. To obtain the reactions of phosphoric acid in the substance under examination is no proof that phosphorus has been administered: for this acid is contained in the majority of animal substances which are used as food. Neither can any reliance be placed upon obtaining the reactions of phosphorous acid in the distillate.

3. **Examination for Hydrocyanic Acid.**

The characteristic bitter-almond smell of prussic acid is generally perceptible in substances in which hydrocyanic acid or cyanide of potassium are present, even in very small quantities. No certain conclusion, however, as to the absence of the poison can be drawn from the absence of the smell.

The best method of detecting prussic acid in cases of poisoning is to separate it from the organic matter in which it is contained by distillation with dilute sulphuric acid. This operation is best performed in a flask, the delivery-tube of which dips into a receiver containing distilled water, in which the hydrocyanic acid (if present) will be completely condensed. A portion of the distillate is neutralised with potash, and tested by a ferroso-ferric salt and hydrochloric acid: another portion is tested by sulphide of ammonium and a ferric salt (p. 41). If the presence of hydrocyanic acid be thus proved, it is still necessary to ascertain whether the cyanogen was contained in the substance examined in the form of some non-poisonous compound — *e. g.* ferro- or ferricyanide of potassium — from which it would be separated as hydrocyanic acid by distillation with sulphuric acid. If this be the case, the aqueous extract of the original substance will give a precipitate of prussian blue with a ferroso-ferric salt.

It must be borne in mind that mixtures which do not contain any cyanide occasionally give off hydrocyanic acid when distilled with sulphuric acid.

4. Examination for Poisonous Organic Bases.

The following are the natural organic bases to which, on account of their poisonous properties, attention must be directed in chemico-legal investigations, and for whose detection a general method of proceeding can, within certain limits, be laid down:

Nicotine, $C^{10}H^{14}N^{2}$. *Coniine*, $C^{8}H^{15}N$. *Strychnine*, $C^{21}H^{22}N^{2}O^{2}$. *Brucine*, $C^{23}H^{26}N^{2}O^{4}$. *Morphine*, $C^{17}H^{19}NO^{3}$. *Atropine* (daturine), $C^{17}H^{23}NO^{3}$. *Hyoscyamine. Solanine. Veratrine*, $C^{32}H^{52}N^{2}O^{8}$. *Colchicine. Aconitine*, $C^{30}H^{47}NO^{7}$.

The following are the principal properties and reactions of these substances. *Nicotine* and *Coniine* are oily liquids, which can be distilled without decomposition: the former boils at 250°, the latter at 170°—200°. They have an offensive smell, which in the case of nicotine is first perceptible on the application of heat. They are readily soluble in alcohol, ether, and acids: their salts are not crystallisable, are soluble in alcohol, insoluble in ether. Nicotine is more soluble in water than coniine. The rest of these bases are solid bodies, and (with the exception of veratrine, colchicine, and aconitine) readily crystallisable.—*Strychnine* is very slightly soluble in water, ether, or absolute alcohol: it has an intensely bitter taste. When it is treated with a few drops of concentrated sulphuric acid, and solid bichromate or ferricyanide of potassium, or peroxide of lead, added to the mixture, a magnificent blue colour is produced, which changes gradually to purple, violet, and red: the addition of water changes the colour at once to red, and gradually to yellow. Chlorine gives a white precipitate with strychnine-salts.—*Brucine* is more soluble in water than strychnine; soluble in alcohol, insoluble in ether. With concentrated nitric acid it gives a dark-red colour, which on heating is changed gradually to orange and yellow: the addition of chloride of tin changes the yellow colour to intense violet.—*Morphine* is difficultly soluble in water and ether, readily in alcohol and alkalis. With concentrated nitric acid it gives first a blood-red, then a yellow, colour: with a neutral solution of ferric chloride a blue colour, which changes to green and brown: with iodic acid and starch paste, blue iodide of starch.—*Atropine* (daturine) and *Hyoscyamine*, when applied to the eye of a cat, produce strong dilatation of the pupil: they are soluble in water, alcohol, and ether, forming alkaline solutions.—*Solanine* is difficultly soluble in water, alcohol and ether: it is coloured yellow by concentrated nitric or hydrochloric acid; by sulphuric acid, first yellow, then violet and brown.—*Veratrine* excites violent sneezing: it is difficultly soluble in water, readily in alcohol or ether: sulphuric acid colours it first yellow, then a fine carmine-red: concentrated hydrochloric acid dissolves it, forming a deep violet solution.—*Colchicine* is soluble in water, alcohol, and ether: sulphuric acid colours it brown-yellow; nitric acid, blue or violet, changing to olive-green and yellow.—*Aconitine* is tolerably soluble in boiling water, forming a strongly alkaline solution; readily soluble in alcohol, less so in ether. Nitric acid dissolves it without change of colour: sulphuric acid colours it first yellow, then violet. Like atropine, it produces dilatation of the pupil.—All these bases in a not too dilute hydrochloric acid solution give yellow precipitates with terchloride of gold, bichloride of platinum, and phosphomolybdic acid; and white precipitates with chloride of mercury. Most of them are precipitated white by tannic acid, brown by solution of iodine.

The simplest method for the separation of these bases from the organic matters which are usually submitted to analysis in chemico-legal investigations, is that proposed by Sonnenschein (Ann. Ch. Pharm. civ. 45). The reaction upon which this method of separation is founded is the precipitation of these substances from an aqueous acid solution by *phosphomolybdic acid*. This reagent is thus prepared. The yellow precipitate obtained by adding phosphate of sodium to molybdate of ammonium is well washed, suspended in water, and heated with carbonate of sodium till it is completely dissolved. The solution is evaporated to dryness, and the residue ignited till all ammonia is expelled: if any reduction of molybdic acid take place, the residue is moistened with nitric acid, and again ignited. It is then heated with water, nitric acid added till the solution has a distinctly acid reaction, and the gold-yellow solution thus obtained diluted till 10 parts solution contain 1 part solid residue. It must be carefully preserved from contact with ammonia.

The following is the process for the extraction of the bases. The whole of the organic matter to be examined is repeatedly exhausted with very dilute hydrochloric acid: the extract is evaporated at a heat of 30° to the consistency of a thin syrup, then diluted, and left for some hours in a cool place before filtration. The filtrate is precipitated by excess of phosphomolybdic acid, filtered off, thoroughly washed with water containing phosphomolybdic and nitric acids, and introduced while moist into a flask. Caustic baryta is added, to a distinct alkaline reaction: and the flask having been fitted with a delivery-tube which is connected with a bulb-apparatus containing hydrochloric acid, heat is gradually applied, when the ammonia and volatile organic bases distil over, and are collected in the hydrochloric acid. The residue in the flask (containing the non-volatile bases) is freed from excess of baryta by a current of carbonic anhydride, carefully evaporated to dryness, and extracted with strong alcohol. On evaporating the alcoholic solution, the bases are commonly obtained in a state of such purity that they will at once exhibit their characteristic reactions: occasionally, however, they require to be further purified by recrystallisation from alcohol or ether.

In some cases—*e. g.* in examination for strychnine in large quantities of liquid—it is advantageous to employ animal charcoal, which possesses the property of absorbing several organic bases. The liquid is left for a day in contact with good animal charcoal, being frequently agitated with it: the charcoal is collected on a filter, thoroughly washed, and boiled with alcohol, which dissolves out the base.

The facts elicited by the judicial investigation will generally afford a clue to the particular poison which is especially to be looked for. The reactions obtained should always be controlled by careful comparison with those exhibited by a pure specimen of the substance whose presence is suspected.

ATOMIC WEIGHTS AND SYMBOLS OF THE ELEMENTS.

Sym.	Element.	At. wt.
Al.	Aluminium	13·6
Sb.	Antimony	120
As.	Arsenic	75
Ba.	Barium	68·6
Bi.	Bismuth	208
B.	Boron	14·5
Br.	Bromine	80
Cd.	Cadmium	56
Ca.	Calcium	20
C.	Carbon	12
Ce.	Cerium	46
Cl.	Chlorine	35·5
Cr.	Chromium	26·2
Co.	Cobalt	30
Cu.	Copper	31·7
Di.	Didymium	48
E.	Erbium	—
F.	Fluorine	19
G.	Glucinum or Beryllium	4·7
Au.	Gold	196
H.	Hydrogen	1
I.	Iodine	127
Ir.	Iridium.	98·6
Fe.	Iron	28
La.	Lanthanum	46
Pb.	Lead	103·5
Li.	Lithium	6·5
Mg.	Magnesium	12
Mn.	Manganese	26
Hg.	Mercury	100
Mo.	Molybdenum	48
Ni.	Nickel	29
Nb.	Niobium or Columbium	—
N.	Nitrogen	14
Os.	Osmium	100
O.	Oxygen	16
Pd.	Palladium	53
P.	Phosphorus	31
Pt.	Platinum	99
K.	Potassium	39
Rh.	Rhodium	52
Ru.	Ruthenium	52
Se.	Selenium	79
Si.	Silicium	28·5
Ag.	Silver	108
Na.	Sodium	23
Sr.	Strontium	43·9
S.	Sulphur	32
Ta.	Tantalum	137·6
Te.	Tellurium	128
Tr.	Terbium	—
Th.	Thorium.	59·5
Sn.	Tin	118
Ti.	Titanium	50
U.	Uranium	60
V.	Vanadium	68·5
W.	Wolfram or Tungsten	92
Y.	Yttrium	35
Zn.	Zinc	32·5
Zr.	Zirçonium	22·4

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